

Project 325B

Technical Progress Report

Period: July 1, 1972 to October 15, 1972

Submitted By:

Project Manager

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CHEMICAL R & D: SUMMARY

Sixty-three peroxide/hydroperoxide decomposers have thus far been screened and of this number about 12 appear promising enough for continued evaluation (1.1.1.1).

Formula 5/D8, in every respect, appears to be as good as and in most instances superior to 5/D7. Preliminary over-coating evaluation indicates less rapid spot growth and greater retained sensitivity than 5/D7 (1.1.1.2.1).

The pH of the PVA-overcoat is a critical factor in controlling spot growth (1.1.1.2.2).

Sub-microscopic silica is recognized as a possible cause of spot growth (1.1.1.2.3).

Loss of CBr_4 has been measured by an infrared method which proves to be fairly accurate (1.1.1.3.1).

Attempts to simulate speed decay of 5/D7 films failed. Although an autoxidation mechanism with formation of D260-hydroperoxide remains a viable hypothesis, subsequent decomposition to 4DMAP can no longer be considered the only cause of observed speed decay (1.1.1.3.2).

Ingredient interaction decay studies with 5/D8 indicate superiority of 5/D8 over 5/D7 (1.1.1.3.3).

Coating solution decay studies indicate greater stability for 5/D8 compared to 5/D7 (1.1.1.3.4).

D263 is being evaluated as a substitute for D260. Consideration of the mechanism of chemical speed decay indicates D263 may be less prone to chemical decay than D260 (1.1.3.3).

The period from July 1 through October 15 has been spent investigating and evaluating individual parameters and suspected parameters of spot growth and speed decay. As a result, data indicating any extension of shelf life is not presently available. The second half of this contract period will now include direct collection and evaluation of shelf life data.

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1.1 CHEMICAL R & D

1.1.1 Inhibition of Speed Decay

1.1.1.1 General Screening of Chemical Inhibitors: Peroxide/ Hydroperoxide Decomposers

Mass screening of peroxide/hydroperoxide decomposers began during the first week of September. It comprised addition of additives to Formulas 5 and 5/D7 followed by evaluation of both DPO and RLD modes by comparison to standard controls. To save time, this initial screening did not include overcoating or 5/D8. Evaluation was based upon the effects exhibited on fresh film and on the observed rate of decay over a 24 hour period. Decay was expected if only for the reason that CBr_4 escapes from the film. An additive was therefore considered promising if it showed no detrimental effect on fresh film and showed comparable or preferably less decay than the control.

In the past six weeks, 63 compounds comprising 8 classes have been evaluated by means of this initial screening procedure. The evaluations correspond to the preparation of 1,225 films from 255 coatings, and were performed by three new coating technicians. [] who is in charge of the film evaluation group, and [] the senior technician, are to be commended for their efforts in so effectively training the new technicians in such a short time. 25X1 25X1

The majority of compounds have failed to show any potential, but 12 compounds did show various degrees of promise (marked with an asterisk in Table 1). The classes and compounds, including those yet to be evaluated, are listed in Table 1.

Results to date are summarized as follows:

1. Sulfides

DPO: 5) No apparent effect

5/D7) Slightly higher, reddish fog in 5/D7: sec-
and tert-butyl show slightly higher D_{max} and
 D_{net} than control after 8 hours (Figure 1)

RLD: 5) No effect
5/D7)

- 2 -

TABLE 1

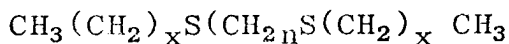
PEROXIDE/HYDROPEROXIDE DECOMPOSERS: Classes and Compounds

Legend: * promising, shown in Figure
() not evaluated

1. Sulfides: R-S-R (Figure 1)

Seven (7) compounds, 28 coating, 140 films

1. n-butyl sulfide
- *2. sec-butyl sulfide
- *3. tert-butyl sulfide
4. n-propyl sulfide
5. isopropyl sulfide
6. phenyl sulfide
7. benzyl phenyl sulfide
8. (methyl phenyl sulfide)



Where,

9. x = 9, n = 3
10. x = 9, n = 4
11. x = 11, n = 2
12. x = 11, n = 4
13. x = 17, n = 2

2. Disulfides: R-S-S-R (Figure 2)

Eight (8) compounds, 32 coatings, 160 films

- *1. n-butyl disulfide
- *2. sec-butyl disulfide
- *3. tert-butyl disulfide
4. n-propyl disulfide
5. isopropyl disulfide
6. phenyl disulfide
7. β -naphthyl disulfide
8. 2,2'-dithiobis (benzothiazole)

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TABLE 1 (continued)

3. Thiolsulfinates: $R-\overset{\overset{O}{\parallel}}{S}-S-R$ (Figure 3)

Six (6) compounds, 24 coatings, 120 films

1. n-butyl thiolsulfinate
- *2. sec-butyl thiolsulfinate
- *3. tert-butyl thiolsulfinate
4. n-propyl thiolsulfinate
5. isopropyl thiolsulfinate
6. phenyl thiolsulfinate

4. Mercaptans: $R-S-R$ (Figure 4)

Four (4) compounds, 16 coatings, 80 films

1. phenyl mercaptan
- *2. 2-mercaptobenzothiazole
- *3. 2-mercaptobenzoxazole
4. 2-mercaptobenzimidazole
5. β -naphthyl mercaptan

5. Metal Xanthates: $M^{+n} (S-\overset{\overset{S}{\parallel}}{C}-OR)_n$

Nine (9) compounds, 36 coatings, 150 films

1. potassium n-propyl xanthate
2. potassium isopropyl xanthate
3. potassium n-butyl xanthate
4. zinc n-propyl xanthate
5. zinc isopropyl xanthate
6. zinc n-butyl xanthate
7. cupric n-propyl xanthate
8. cupric isopropyl xanthate
9. cupric n-butyl xanthate

6. Sulfoxides: $R-\overset{\overset{O}{\parallel}}{S}-R$ (Figure 5)

Ten (10) compounds, 44 coatings, 210 films

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TABLE 1 (continued)

6. Sulfoxides: (continued)

1. n-butyl sulfoxide
- *2. sec-butyl sulfoxide
3. tert-butyl sulfoxide
4. n-propyl sulfoxide
- *5. isopropyl sulfoxide
6. phenyl sulfoxide
7. benzyl sulfoxide
8. dimethyl sulfoxide
9. dilauryl β, β' -sulfinyldipropionate
10. distearyl β, β' -sulfinyldipropionate

7. Sulfones:
$$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{S}-\text{R} \\ \parallel \\ \text{O} \end{array}$$
 (Figure 6)

Seven (7) compounds, 28 coatings, 140 films

1. n-butyl sulfone
2. sec-butyl sulfone
- *3. tert-butyl sulfone
4. n-propyl sulfone
5. isopropyl sulfone
- *6. phenyl sulfone
7. methyl sulfone

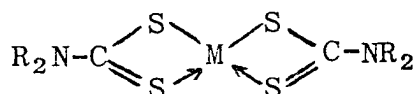
8. Metal Dialkyl Dithiophosphonates:
$$\begin{array}{c} \text{S} \\ \parallel \\ \text{M}^{+n} \{ \text{S}-\text{P}(\text{OR})_2 \}_2 \end{array}$$

Twelve (12) compounds, 47 coatings, 225 films

1. potassium di-n-propyl dithiophosphonates
2. potassium diisopropyl dithiophosphonates
3. nickel di-n-propyl dithiophosphonates
4. nickel diisopropyl dithiophosphonates
5. bismuth di-n-propyl dithiophosphonates
6. bismuth diisopropyl dithiophosphonates
7. zinc di-n-propyl dithiophosphonates
8. zinc diisopropyl dithiophosphonates
9. cupric di-n-propyl dithiophosphonates
10. cupric diisopropyl dithiophosphonates
11. cadmium di-n-propyl dithiophosphonates
12. cadmium diisopropyl dithiophosphonates

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TABLE 1 (continued)

(N,N-Disubstituted Dithiocarbamates):

1. zinc dimethyldithiocarbamate
2. zinc dibenzoyldithiocarbamate
3. zinc diethyldithiocarbamate
4. zinc dibutyldithiocarbamate
5. zinc ethylenebisdithiocarbamate
6. nickel dimethyldithiocarbamate
7. nickel dibutyldithiocarbamate
8. nickel pentamethylenedithiocarbamate
9. nickel cyclopentamethylenedithiocarbamate
10. cadmium cyclopentamethylenedithiocarbamate
11. bismuth dimethyldithiocarbamate
12. lead dimethyldithiocarbamate
13. lead diethyldithiocarbamate
14. sodium dimethyldithiocarbamate
15. sodium diphenyldithiocarbamate
16. phenyl mercuric dimethyldithiocarbamate
17. bis(dimethylthiocarbamyl)sulfide
18. bis(dimethylthiocarbamyl)disulfide

(Thiosulfenyl Xanthates):

$$\text{R}-\text{S}-\text{S}-\overset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{OR}$$

1. O-ethyl S-n-butylthiosulfenyl xanthate
2. O-ethyl S-sec-butylthiosulfenyl xanthate
3. O-ethyl S-t-butylthiosulfenyl xanthate
4. O-ethyl S-phenylthiosulfenyl xanthate

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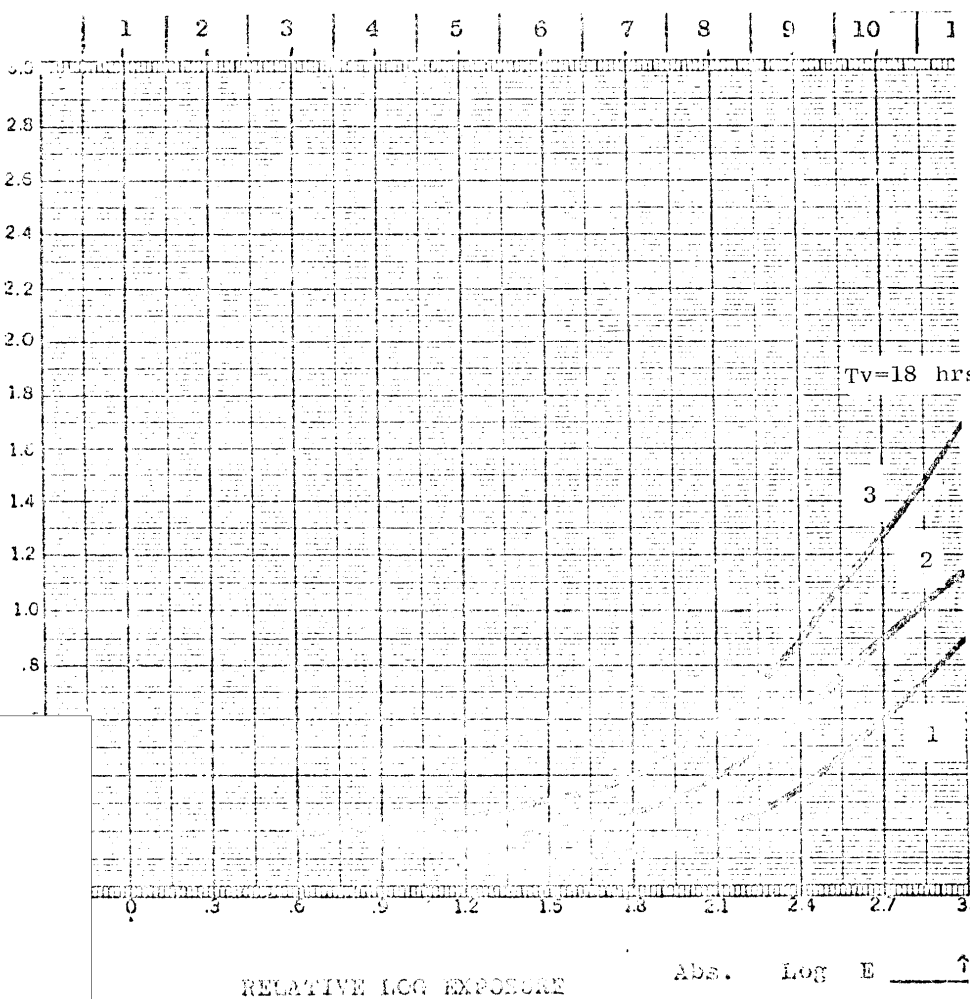


FIGURE 1

Screening of Peroxide/Hydroperoxide Decomposers:

Sulfides at 24 Hours

1. 5/D7 Control
2. t-butyl sulfide
3. sec-butyl sulfide

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1

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2. Disulfides

DPO: 5) No effect

5/D7) Tendency toward lower fog after 24 hours; n-,
sec- and tert-butyl show slightly higher D_{net}
than control after 24 hours (Figure 2)RLD: 5)
5/D7) No effect3. ThiolsulfinatesDPO: 5) Higher initial fog and higher rate of fogging
during aging5/D7) Similar to control but with higher reddish fog;
sec- and tert-butyl show slightly higher D_{max}
with comparable fog to control after 24 hours
(Figure 3)RLD: 5)
5/D7) Destroy imaging of fresh films4. Mercaptans

DPO: 5) Slightly lower fog on aging

5/D7) Better than control; the benzothiazole and
benzoxazole show much higher D_{net} with only slightly
higher fog (Figure 4)RLD: 5)
5/D7) No or only slight imaging in fresh film5. Metal Xanthates

DPO: 5) Higher fog, lower densities in fresh film

5/D7) Potassium and copper salts show very high fog in
fresh films and larger increase on aging; zinc
salts show no fog in fresh film but rapid increase
on aging.RLD: 5)
5/D7) No imaging at all

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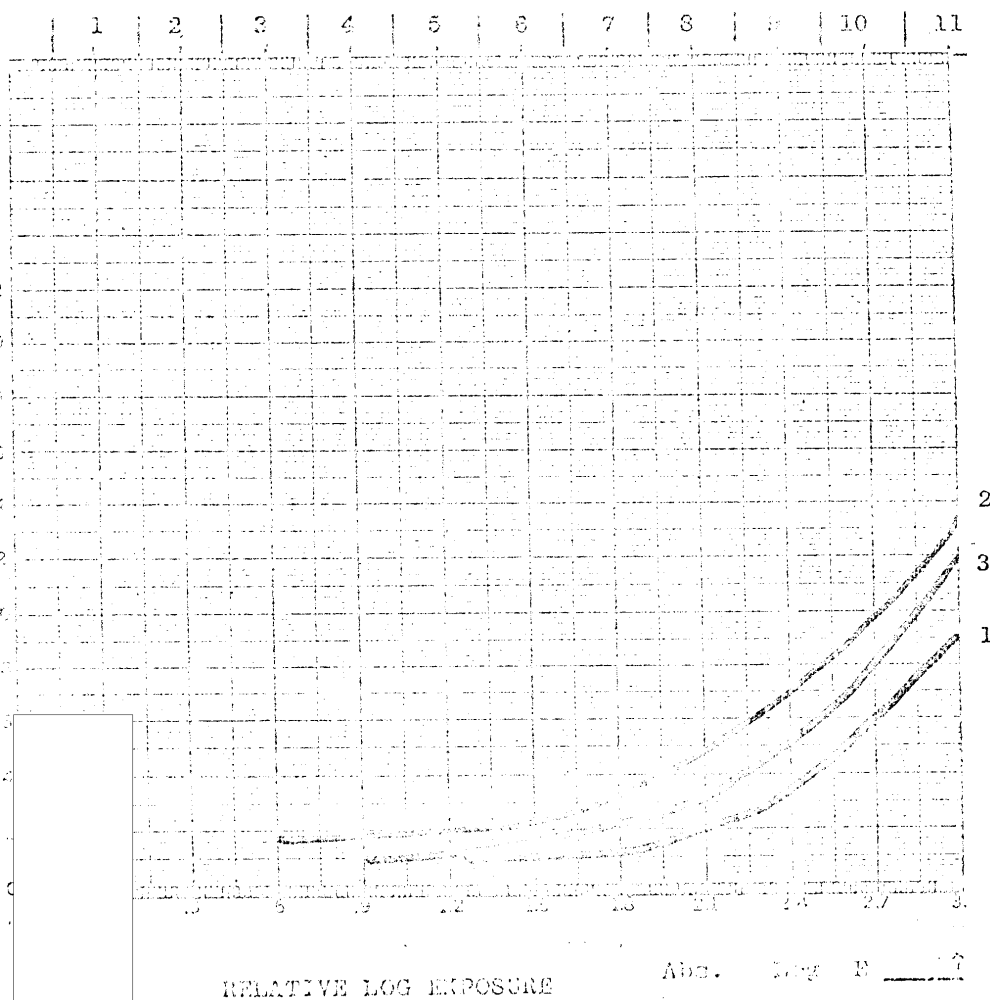


FIGURE 2
DISULFIDES (Tv = 24 Hrs.)

1. 5/D7 Control
2. n-butyl disulfide
3. sec-butyl disulfide
3. t-butyl disulfide

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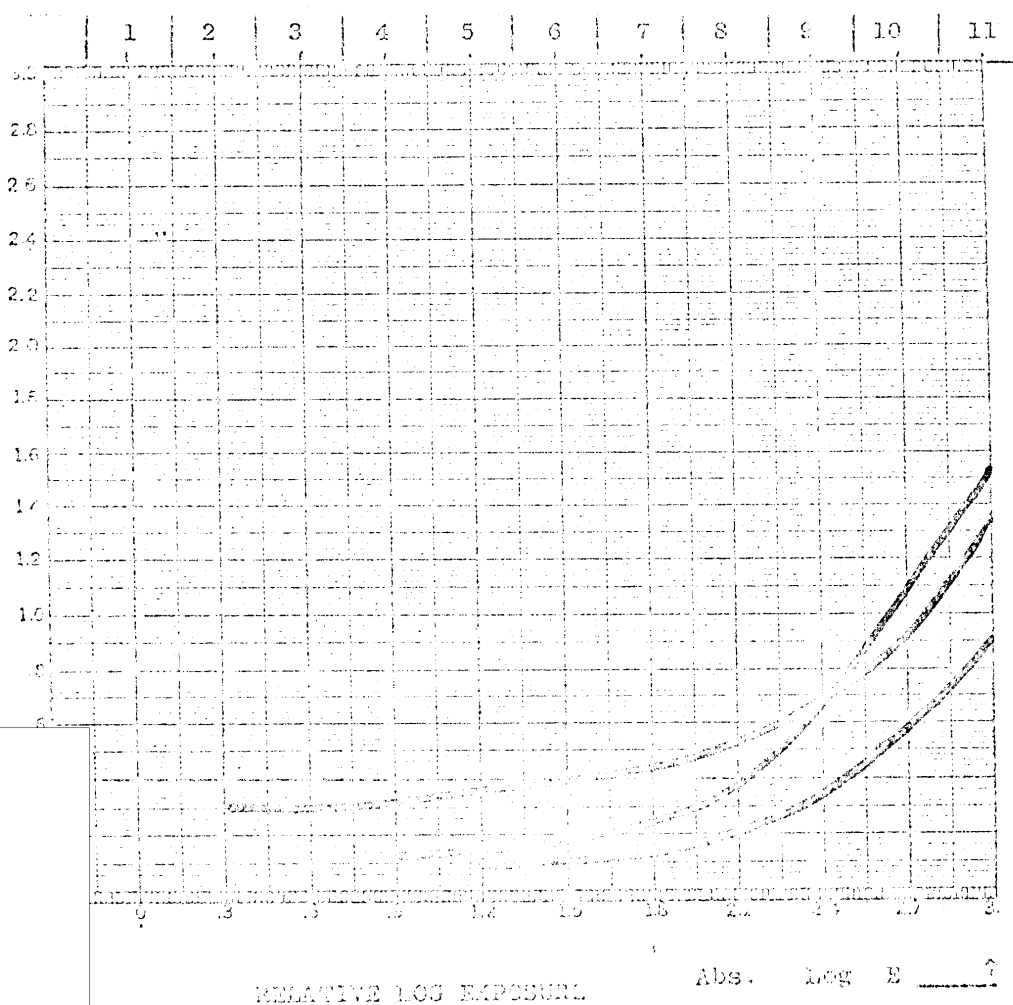


FIGURE 3

Thiol sulfinates (Tv =

1. 5/D7 Control
2. sec-butyl thiol sulfinates
3. t-butyl thiol sulfinates

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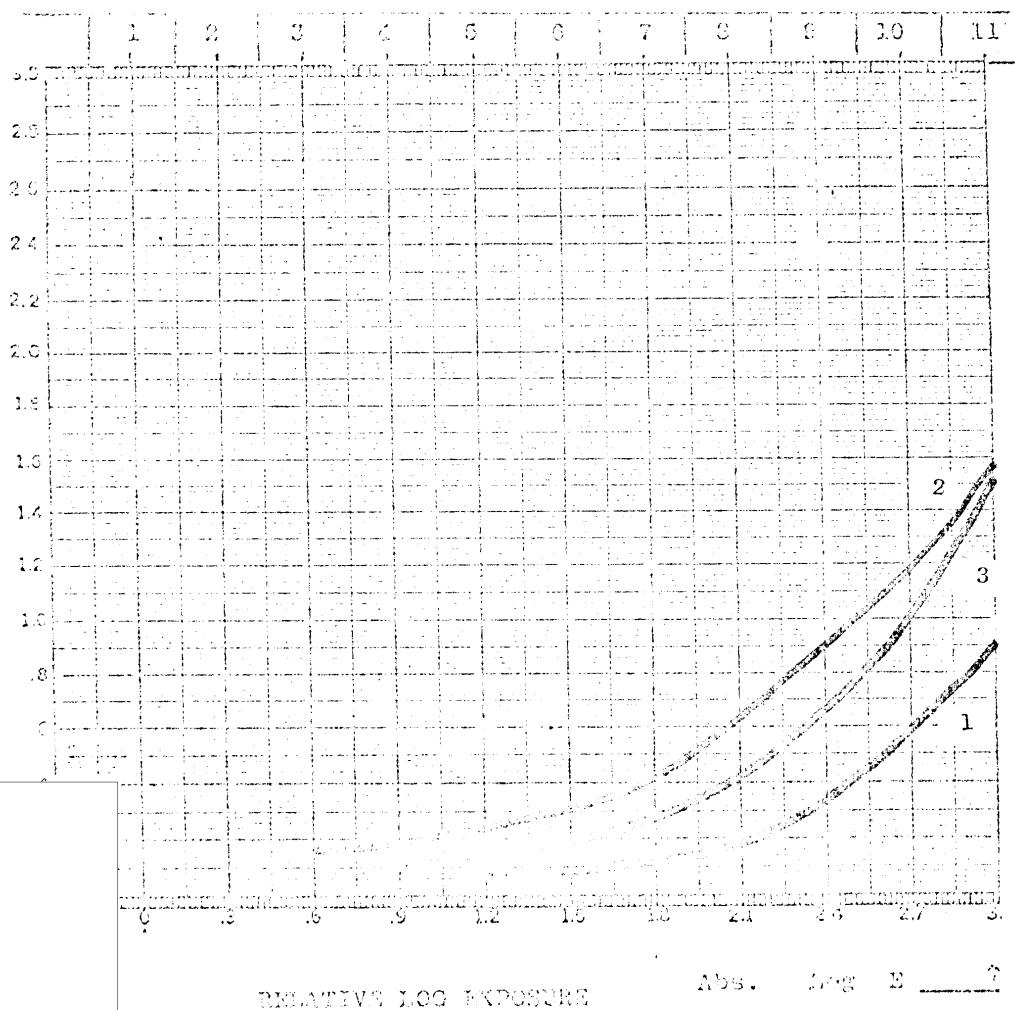


FIGURE 4

Mercaptans (Tv = 24 Hrs)

1. 5/D7 Control
2. 2-mercaptobenzoxazole
3. 2-mercaptobenzothiazole

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25X1

- 11 -

6. Sulfoxides

DPO: 5) No effect
 5/D7) Similar to control with less fogging on aging
 (Figure 5)
RLD: 5)
 5/D7) No effect

7. Sulfones

DPO: 5) No effect
 5/D7) Similar to control with less fogging on aging;
 phenyl and t-butyl are best (Figure 6)
RLD: 5)
 5/D7) No effect

8. Metal Dialkyl Dithiophosphonates

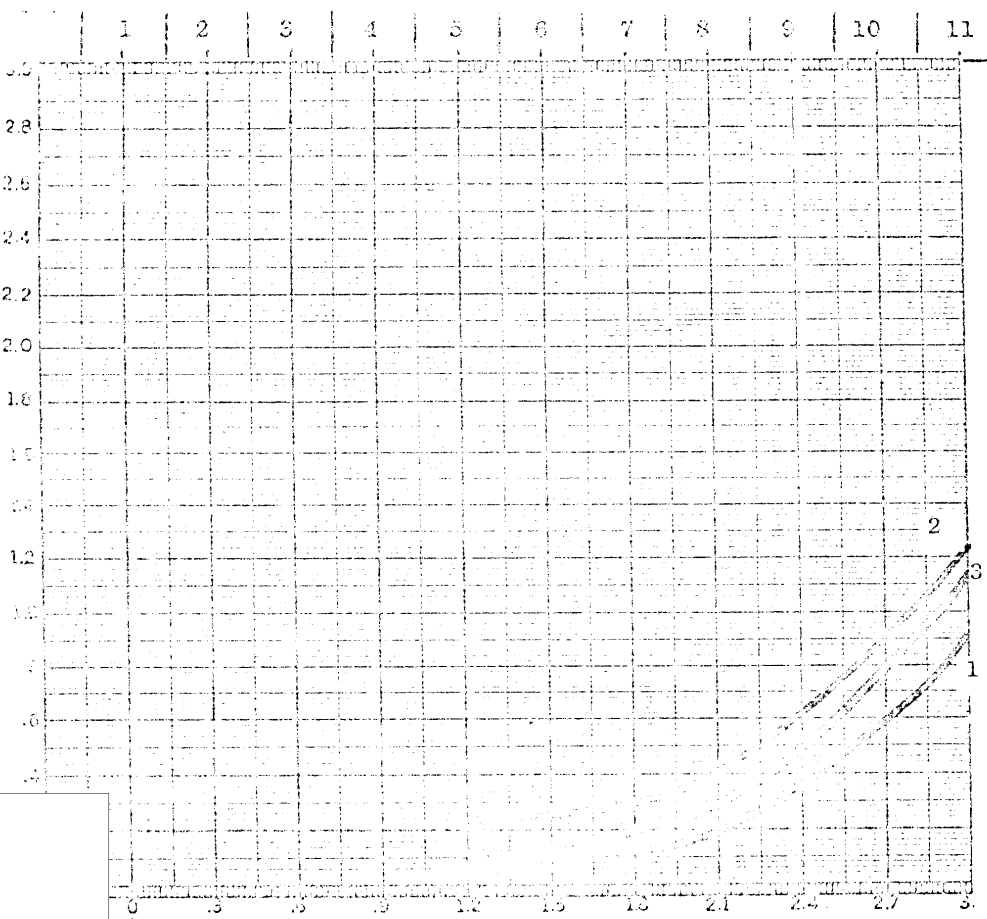
DPO: 5) No or only slight imaging with no fog
 5/D7) Same
RLD: 5)
 5/D7) No imaging or fogging

Formula 5 has been of little value in evaluating these additives. It is therefore being dropped and 5/D8 is being substituted in its place.

1.1.1.2 Combined Chemical/Overcoating Methods1.1.1.2.1 Formula 5/D8

In the autumn of 1970 formulation studies had led to the development of Formula 5 and the discovery that addition of D7 (5/D7) would produce the desired AEI speeds. D8 was also found fairly effective but speeds were at best only about one-half those produced by D7¹. Studies of 5/D7 were therefore emphasized and as a result of subsequent tasks (once the desired AEI speed had been demonstrated) and as a result of a number of material-failures, there was never sufficient time for further investigations of Formula 5/D8.

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RELATIVE LOG EXPOSURE

Abs. Log E \uparrow

FIGURE 5

Sulfoxides (Tv = 24

1. 5/D7 Control
2. isopropyl sulfoxide
3. sec-butyl sulfoxide

- 12 -

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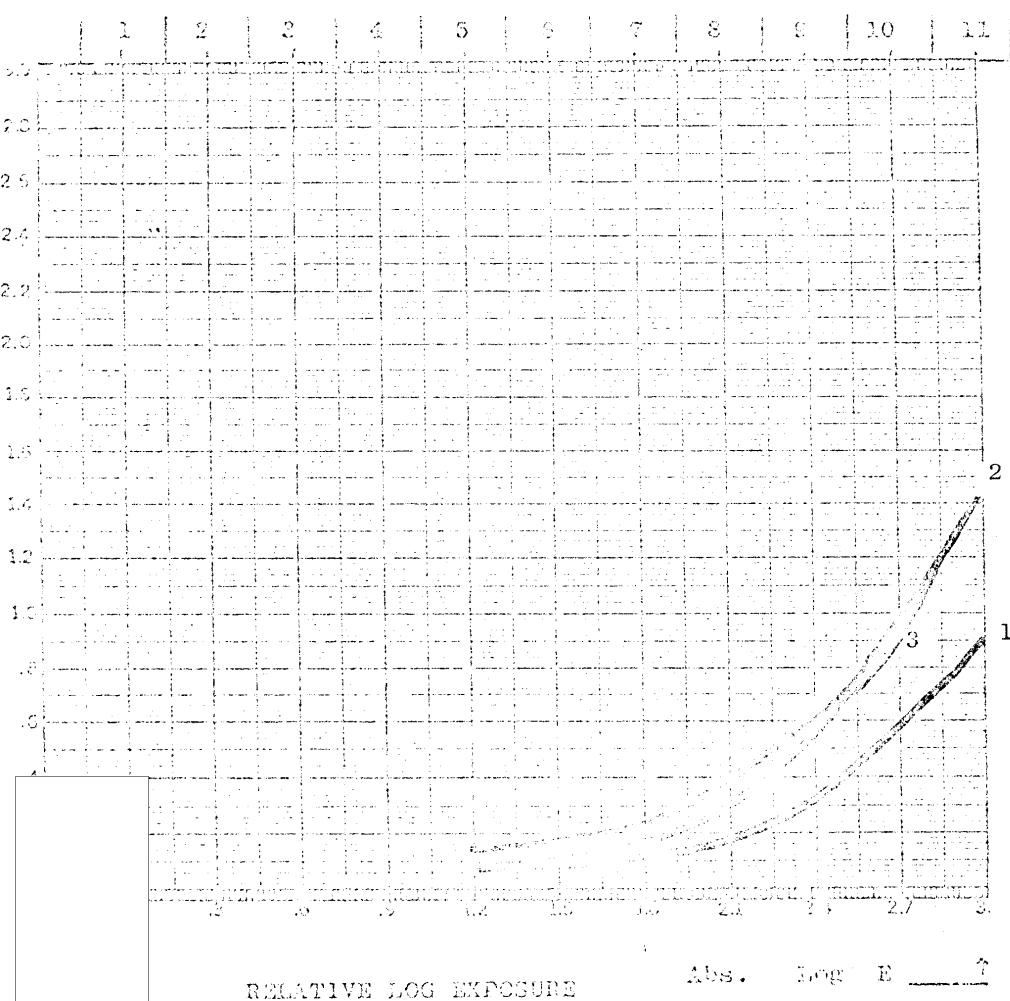


FIGURE 6
Sulfones (Tv = 24 Hr.)

1. 5/D7 Control
2. t-butyl sulfone
3. phenyl sulfone

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25X1

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The current considerations of shelf-life/speed decay and system nonuniformities again led to a consideration of 5/D8, primarily as a means of evaluating the role of D7, which is the suspected cause of blotching and a primary suspect in speed decay, as a result of ingredient interaction decay studies².

Formulation studies have quickly led to the conclusion that 5/D8 is a more desirable system than 5/D7. The first indication of superiority resulted from attaining AEI speeds of 3 to 8 almost from the beginning. Furthermore, the D-Log E curves were much better behaved than 5/D7 (Figure 7) and curve shapes for RLD and DPO were nearly identical (Figure 8).

Comparison of absorption spectra for unfixed DPO films of 5/D7 (Figure 9) and 5/D8 (Figure 10) at low, medium and high densities indicate that more image dye is formed in 5/D8 than in 5/D7, and this is still more impressive when one realizes that the optimum level of D8 is only two-thirds the level of D7. D8-dye is blue and adds to the green-red portion of the spectrum as does D260-dye (D392). As a result maximum densities are read with the Wratten 93 (green) filter in the MacBeth TD-102 densitometer. In contrast, D7-dye is read and 5/D7's maximum densities are read with the Wratten 94 (blue) filter. The maximum densities read for 5/D8 are only 2.0 (compared to 2.7 for 5/D7) and are inconsistent with the absorption spectra shown in Figure 10. We have recently discovered that the Quantascan Recording densitometer using a Wratten 93, gives density readings as high as 4.0 (Figure 8) which are consistent with Figure 10. There is presently no explanation for the failure of the TD-102 densitometer to record these higher densities but regardless, we now know that 5/D8 has a DLE range as good or better than 5/D7.

Comparison of Figures 9 and 10 also shows higher absorption in the 650-700 nm region for 5/D8 and suggests that optimum development might be at longer wavelength than that for 5/D7. Preliminary studies show the optimum wavelength is between 683 and 707 nm compared to 650 to 675 for 5/D7. Furthermore, PVA-overcoated film develops with still longer wavelength, in the vicinity of 717 nm. The capability of developing 5/D8 with longer wavelength will be necessary for extending spectral sensitivity to 680 nm.

Figure 11 compares the absorption spectra of unexposed 5/D7 and 5/D8. The spectra are similar but note the greater absorbance of 5/D8 (with less D8 than D7) in the 300 to 650 nm region. Some degree of enhanced sensitivity had been expected on the assumption that the charge-transfer complexes of D7 and D8 with CBr_4 assume some of the character of their respective

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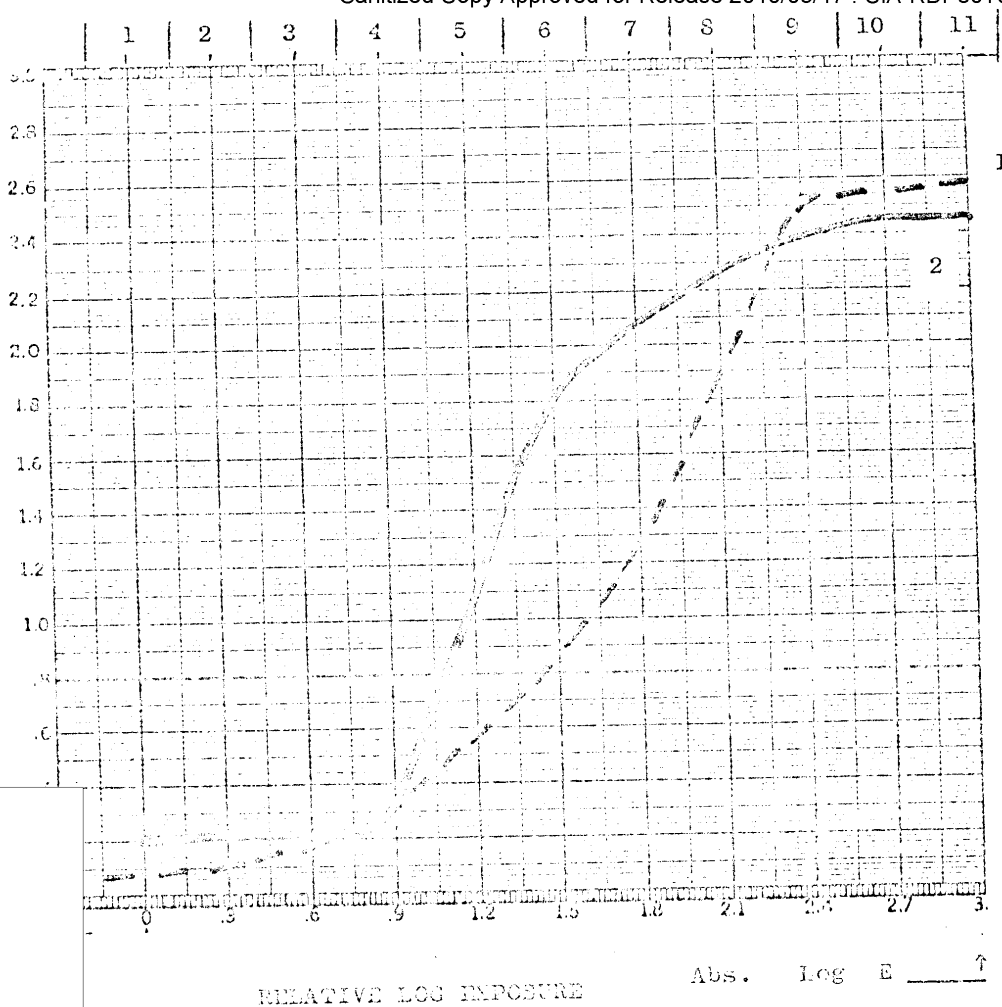


FIGURE 7
TYPICAL RLD AND DPO CURVES
for
FORMULA 5/D7

- 1. DPO
- 2. RLD

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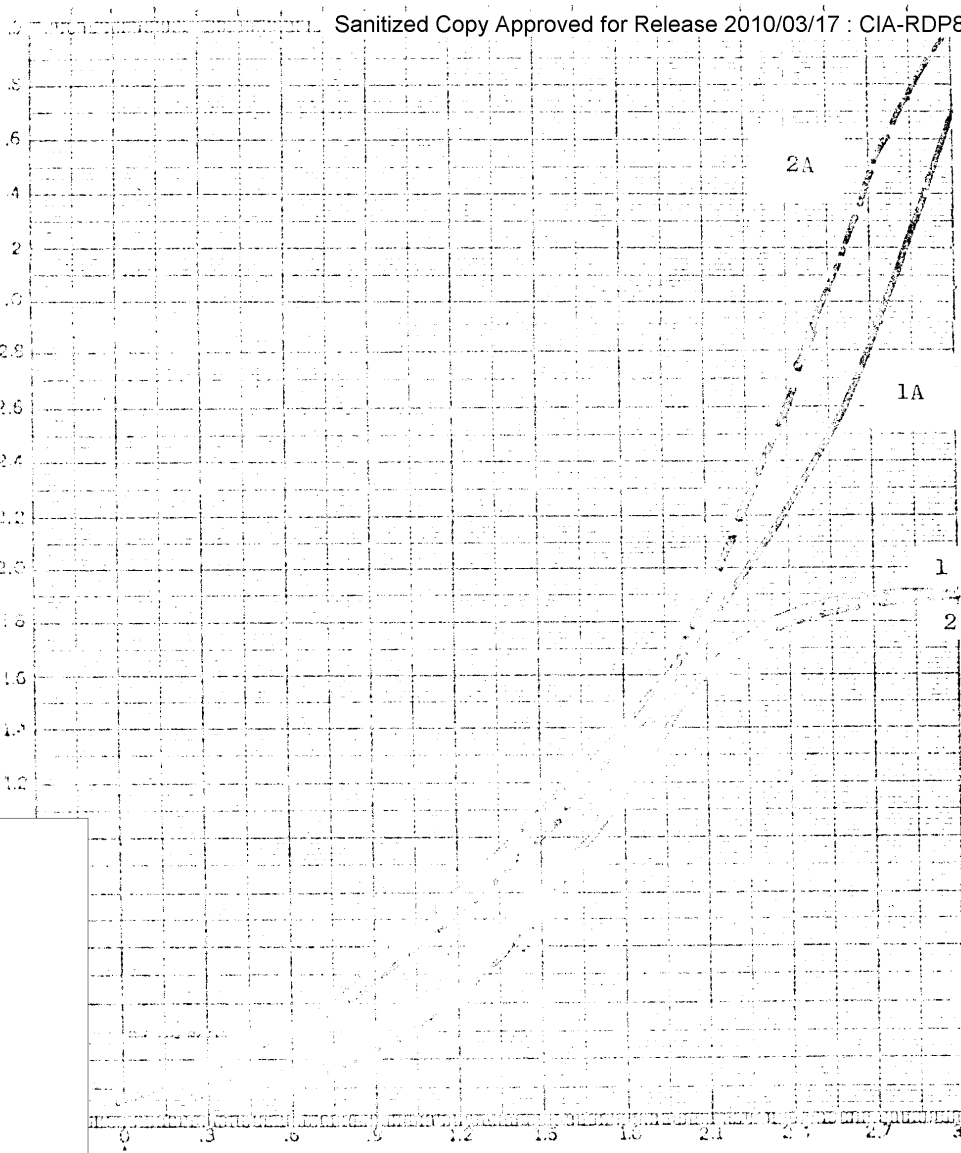


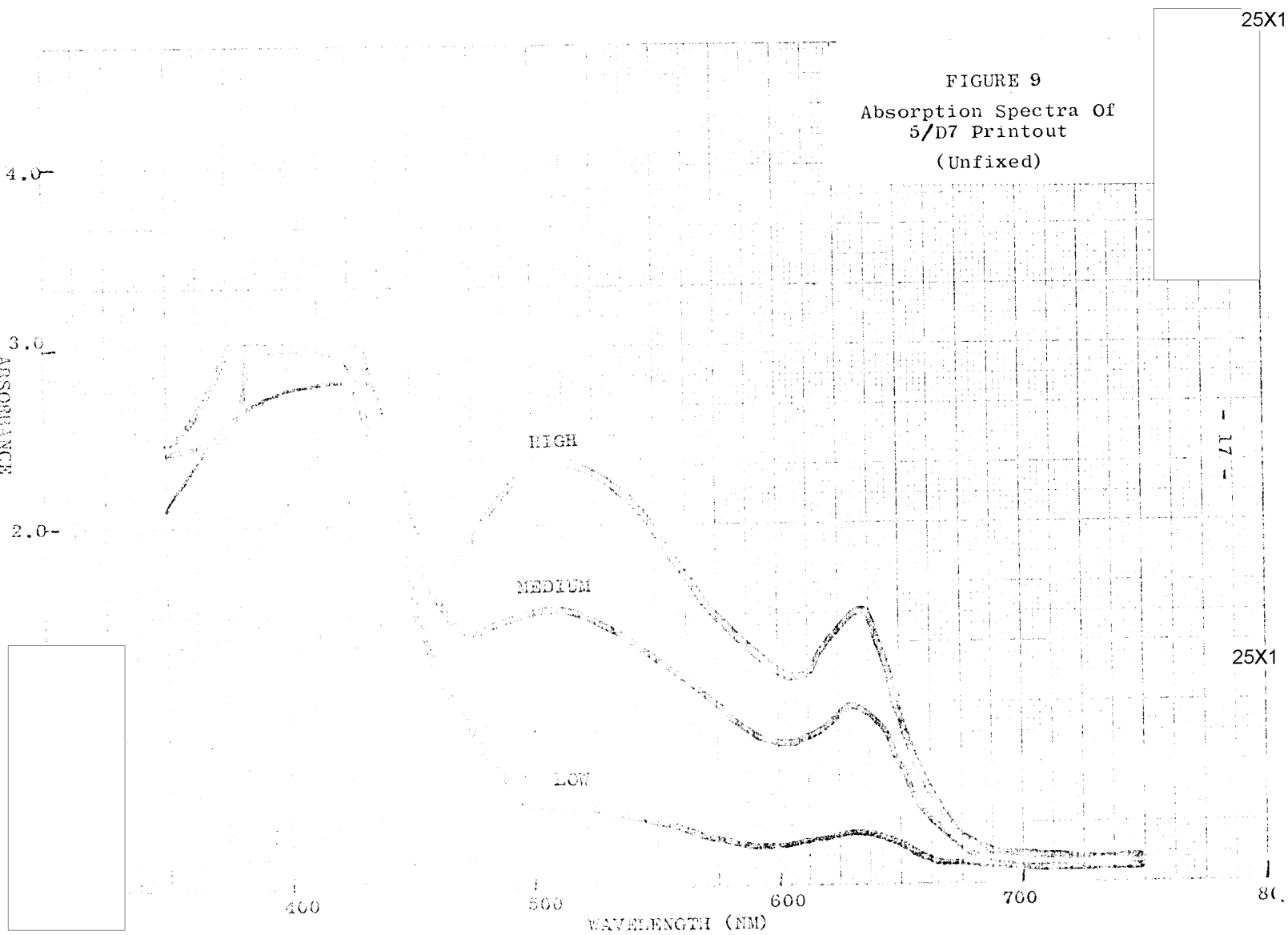
FIGURE 8
RLD and DPO Curves
for
FORMULA 5/D8

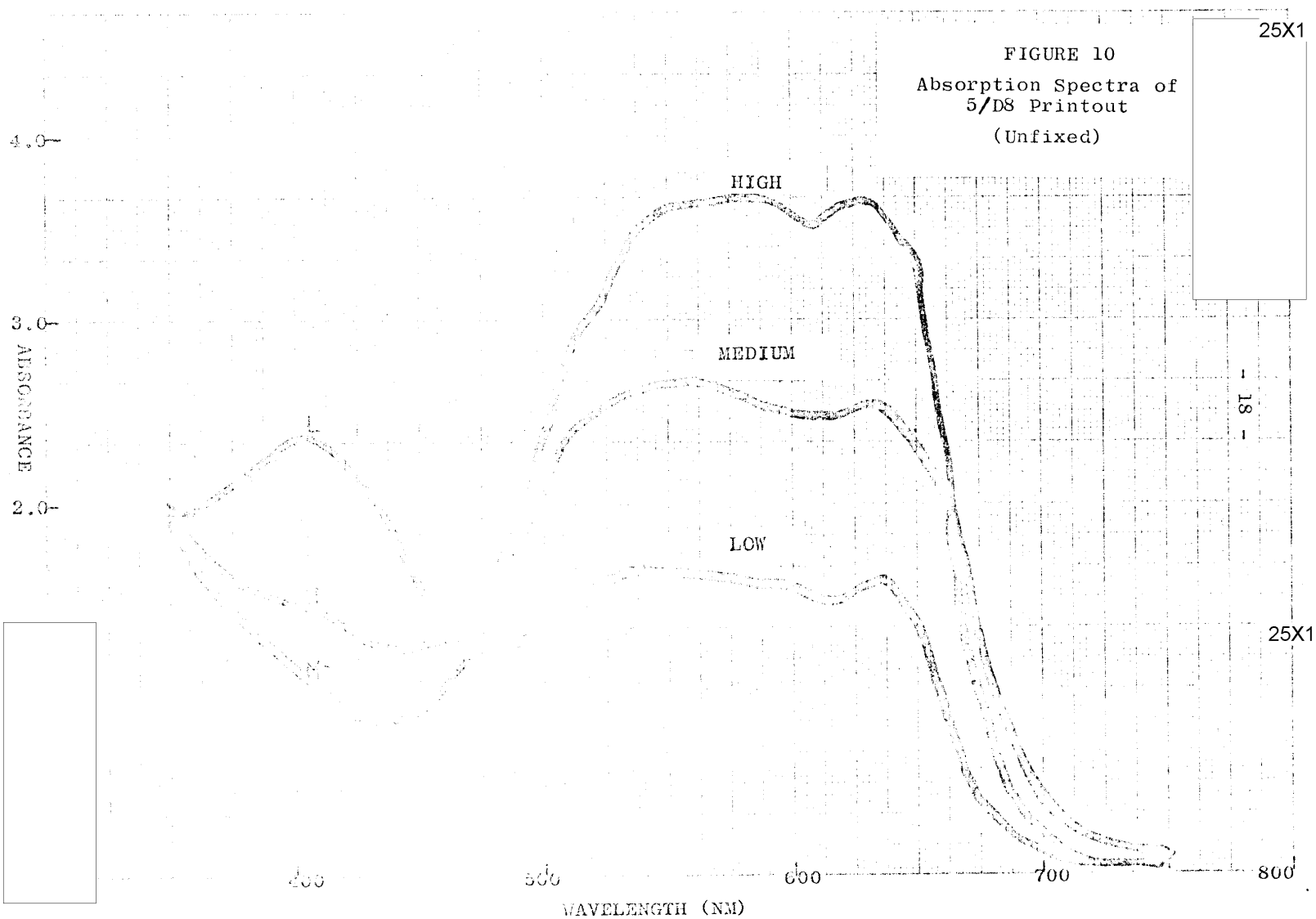
- 1. DPO - Read on MacBeth Densitometer
- 1A. DPO - Read on Recording Densitometer
- 2. RLD - Read on MacBeth Densitometer
- 2A. RLD - Read on Recording Densitometer

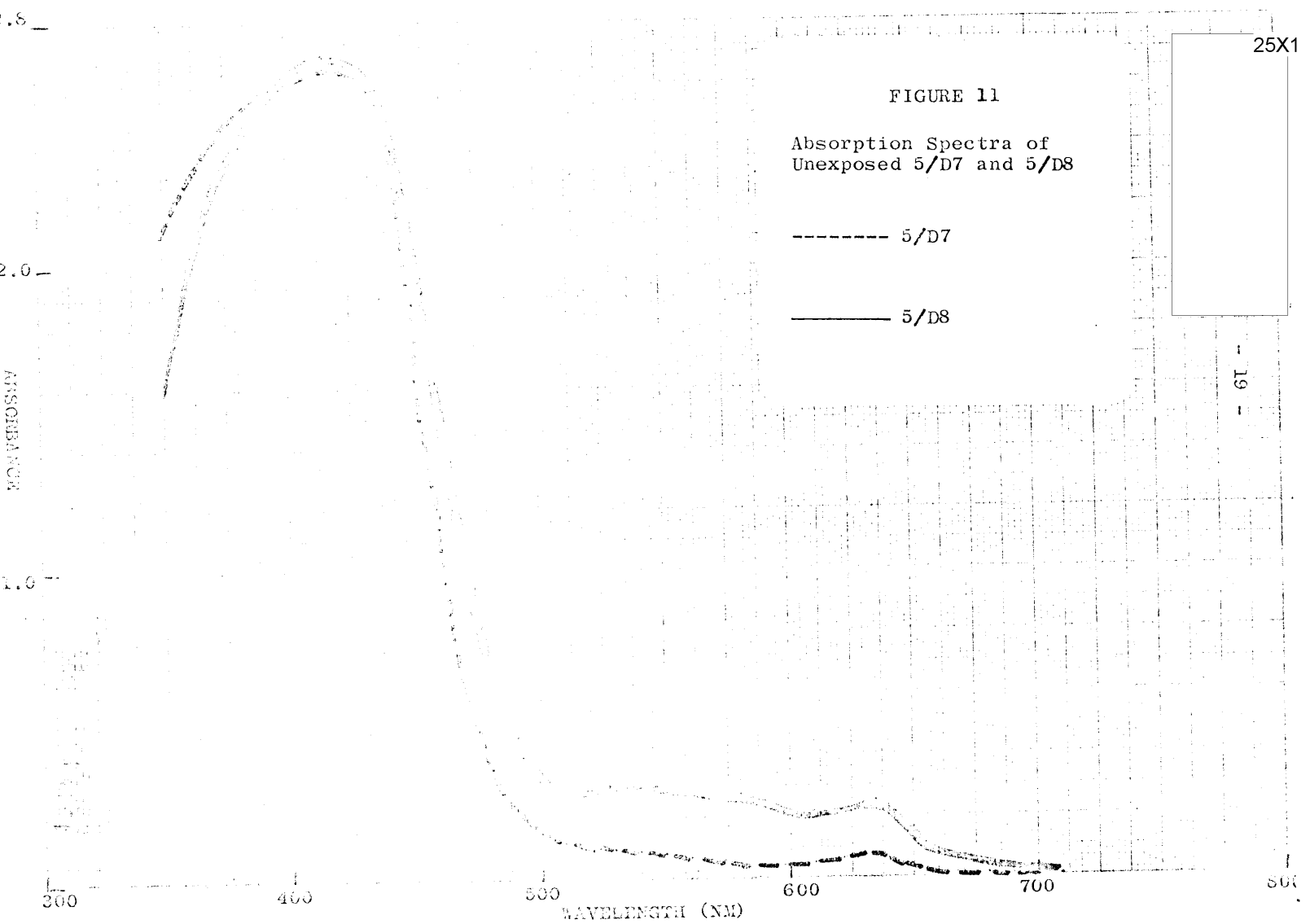
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- 20 -

dyes. D8 absorbs at 400 nm and its dye at 528 nm; D7 absorbs at 390 nm and its dye at 496 nm. In order not to detract from our main objective of solving the shelf-life/speed decay problem we have not measured the spectral sensitivity of 5/D8. We do expect to find that 5/D8 has better red sensitivity than 5/D7 when the spectral sensitivity curves are eventually compared.

A principal cause of spot growth in PVA overcoated films was found to be undissolved crystals. The center of each spot is always found to have a yellow or white crystal, presumably D7 or 4PO respectively. These two ingredients are the least soluble ingredients of the formulation. D8 is more soluble than D7 and, furthermore, its optimum concentration is only two-thirds that of D7. We found that N5 (4-ethyl-3-methylpyridine-N-oxide) is more soluble than 4PO (4-picoline-N-oxide) and that the addition of 20% ethyl acetate (by volume of benzene) apparently enhances the solubility of all ingredients. Finally, we found that with a PVA-overcoat the optimum concentration of N-oxide is increased, and such an increase requires more soluble N-oxides like N5 if spot growth is to be arrested. Advantage was taken of these facts by combining them into a new formulation, Formula 10. As a result a PVA-overcoated film lasted 27 hours at 70°C without spot growth and without loss of DPO sensitivity (RLD mode was not checked). After 21 hours a new type of random spot growth occurred. The spots were distinctly different than those caused by crystals and looked like amoebas under the microscope. It is believed these spots may be a result of chemical reaction between the aqueous overcoat and the photosensitive layer. One possibility is reaction between water and CBr_4 to produce acid. A second possibility is diffusion of the more water-soluble N-oxide from the photosensitive layer to the overcoat since the film is known to fog more readily as the concentration of N-oxide is decreased. Still another possibility has to do with the pH of the overcoat which will be discussed in the next Section.

Recently, studies began with screening in 5/D8 many of the N-oxides which were previously screened with 5 and 5/D7. Some more recently synthesized N-oxides (see Section 1.1.3.4) have greater solubility in benzene. Preliminary results which were available only as this report was being written indicate that some N-oxides which proved to be of no value and even detrimental to 5/D7 are affording superior results than either 4PO or N5, including retardation of speed decay.

Additional evidence supporting the superiority of D8 is found in ingredient interaction decay studies of 5/D8 Section 1.1.1.3.3, and comparisons of coating solution decay of 5/D8 and 5/D7, Section 1.1.1.3.4.

25X1

- 21 -

The preceding facts form the basis for concluding that 5/D8 cannot be neglected in the search for a final solution to the speed decay problem. Unfortunately, time and resources prevent performing all experiments with both 5/D7 and 5/D8. Work will continue with 5/D7 but more emphasis is now being placed on 5/D8. This decision is based primarily on the realization the retardation of spot growth, with little or no loss of sensitivity, was accomplished without employing many of the sophisticated coating techniques developed by Engineering and employed in the previously reported results of overcoated 5/D7. In addition to all the apparent advantages of 5/D8 mentioned above, this one fact seems most immediately important in concluding that the best chance for solution to the speed decay problem lies with Formula 5/D8.

1.1.1.2.2 pH of the PVA-Overcoat

The pH of the polyvinyl alcohol (PVA) overcoat layer was varied from 3 to 13 with aqueous hydrochloric acid and six bases. Before treatment, the pH of the control PVA, which had been slurried with ion exchange resin, was 5.6 (cf. Section 1.1.5.3).

This low pH (acidic) may cause D7 or D8 dye-formation. Too high a pH (basic) may interfere with D7 or D8 dye-formation, however. The optimum pH was found to be on the basic side: 9 to 11. The trialkylamines work best. At this stage in the investigation tributylamine at pH 9 is the best found: Dmax, γ , and speed are similar to the control and there are fewer spots. Triethylamine at pH 9 is almost as good, with somewhat lower gamma and more spots. It is not likely to give as good long term stability as tributylamine because of its higher volatility. In fact, tributylamine is the least volatile trialkylamine which has sufficient solubility to produce pH of 9 in the PVA overcoat.

When the overcoat was acidified to 3 or 5 with hydrochloric acid the films dark-fogged after 1 to 3 hours. Basification with DABCO or sodium hydroxide caused many spots; basification with triethanolamine led to completely fogged film. Best results were obtained at pH 9 and 11 with tributylamine, triethylamine, and tetramethylammonium hydroxide. The latter, although almost as good as the trialkylamines, did cause some bleeding. Triethylamine at pH 7 resulted in too many spots.

1.1.1.2.3 Possible Role of Silica in Spot Growth

25X1

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Spot growth is the main problem in determining shelf-life with overcoated 5/D7 and 5/D8 films. All coating solutions are filtered through a 5μ filter, yet small spots appear on aging and continue to grow. At 17 hours aging, spots of 10 to 15 mm diameter are sometimes seen.

Microscopic examination of the spots shows several types. One type is apparently due to a crystal of pyridine oxide making a water-sensitive spot. The coating is leached away by the water used to remove the overcoat, resulting in a colorless spot devoid of image.

Dark spots usually have a crystalline center, which is either D7 or D8. Apparently the image precipitates out of solution and crystallizes onto some crystal nucleating agent. In some cases the nucleating agent is readily identifiable under the microscope as a large yellow crystal of D7 or D8, a white crystal of 4PO, or a lint fiber. More often, no identifiable form is evident on microscopic examination. It is suggested that these spots have been nucleated by small solid particles which pass the 5μ filter. It is further suggested that these small particles are room dust and/or glass. Room dust is being controlled much better in the new darkrooms, yet the spots persist. Glass dust is a very likely suspect. Until very recently all of the ingredients (CBr_4 , D260, D7, D8, 4PO, N5) have been purified in our laboratories using sintered Pyrex funnels. In addition, D7 and D8 have been ground in ceramic mortars and pestles. Both procedures present the possibility of generating glass or ceramic particles smaller than 5μ .

Spectrographic analysis of D260 and D7 which have been purified in this way show less than 1 ppm silica. This is the limit of detection by this method. If silica were present in 100 mg D260 in the form of uniform 4μ spheres, 1 ppm would allow 1335 spheres to be present. If the particles were 1μ spheres, 1 ppm would represent 33,700 specks. Thus we see that no method of analysis would be able to assure us that film ingredients are completely free of glass particles.

The practical alternative is to regulate the synthesis and purification of film ingredients so as to eliminate or minimize the possibility of glass dust. By the end of this reporting period new preparations of all of the film ingredients (CBr_4 , D260, D7, D8, 4PO, N5) have been completed or are underway, where paper filters have replaced sintered glass and "Diamonite" alumina (hardness 9+) mortar and pestles have replaced ceramic ones for grinding. When all of these dust-free ingredients are assembled and used for overcoated films, an improvement in the number of spots per unit area should be evident if glass dust is a cause.

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1.1.1.3 Related Studies

1.1.1.3.1 Loss of CBr_4 - Determined by Infrared

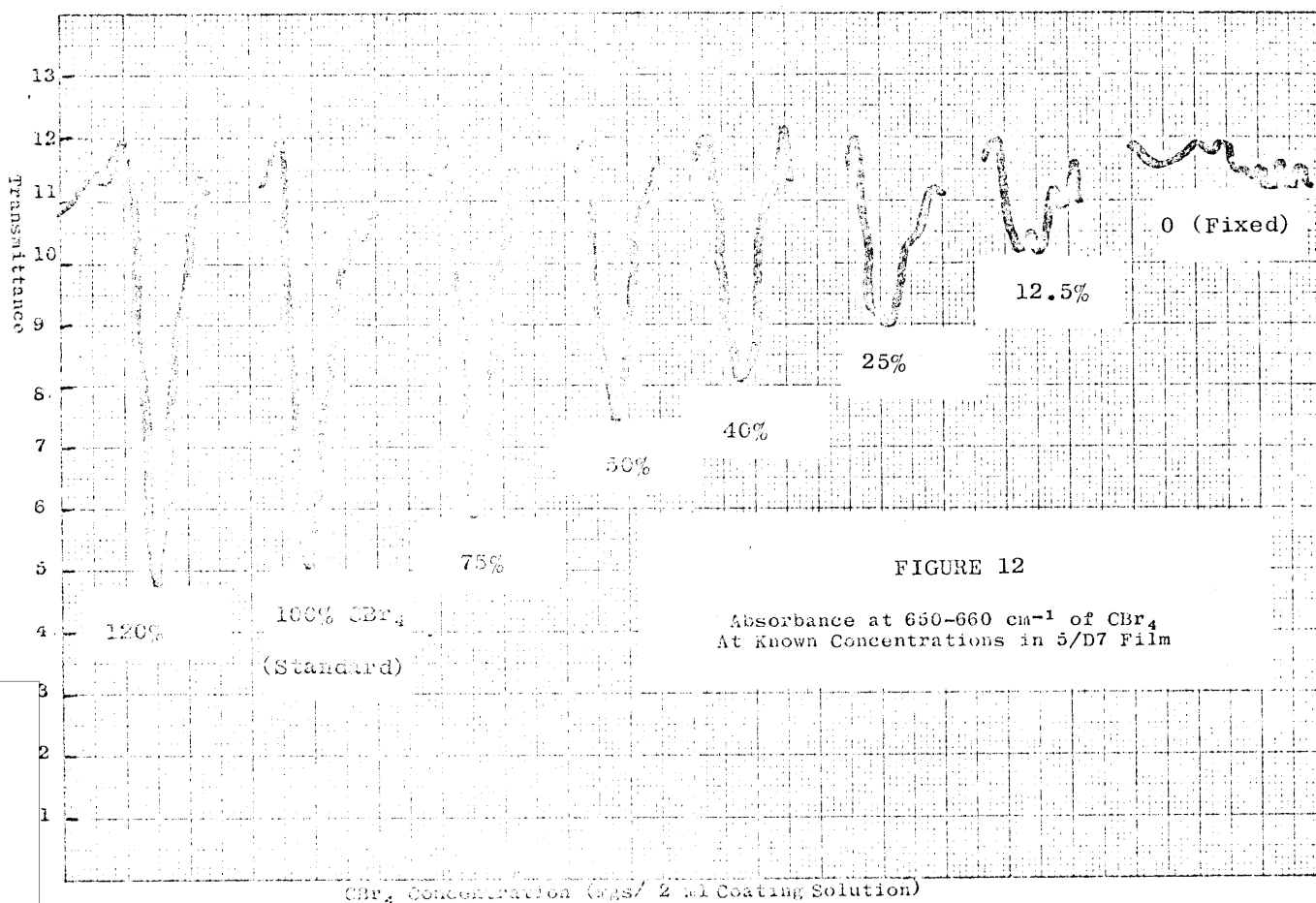
The initial measurements of the CBr_4 loss-rate were based on the absorbance at 625 nm in the 5/D7 film system³. But this method was based upon the tenuous assumptions that this absorbance was due to the charge-transfer complex of D260 with CBr_4 , and was concentration-dependent. The results were consistent with, but did not validate these assumptions. Furthermore, the absorbance was small, absorbance changes were even smaller, and absorbance could change during measurement because of dye formation. Considerable inaccuracy could therefore be expected and an alternate method was desired.

The CBr_4 stretching band is found in the infrared at 650 to 660 cm^{-1} . The infrared absorption peak of standard 5/D7 was compared to films identical in formulation except for the concentration of CBr_4 . Spectra were run on a Perkin-Elmer 457 Infrared Grating spectrophotometer exactly ten minutes after coating. The absorption peaks are seen in Figure 12. Figure 13 shows the absorption of a single piece of film as a function of time. The area under the absorption curve is proportional to the concentration of CBr_4 and assuming negligible loss of CBr_4 during the first ten minutes, the concentrations are known from Figure 12. The actual concentrations of CBr_4 remaining in the film can therefore be determined. The absorption curves are sufficiently symmetrical so peak heights rather than areas were used. Plots of peak heights versus concentrations and peak heights versus time (aged film) are seen in Figure 14. These curves can be used to determine the loss of CBr_4 at any time as indicated by the example shown. The example indicates that about 40% of the initial CBr_4 loading has been lost during the first 5 hours. Note also that the loss of CBr_4 levels off at about 60% after several days.

This method agrees reasonably well with the loss-rate indicated by the visible absorption spectra at 630 nm, which indicates 50% lost in about two hours (Figure 15). The infrared results must be considered more reliable in view of the uncertainties previously mentioned about the visible absorption method. The beauty of the infrared method lies in the fact that measurements are independent of visible absorption; that is, the amount of dye formed in a fogged film, for example.

Accuracy of the infrared method was independently verified by weight-loss measurements with a film which was two weeks old. The measurement of weight loss for determining the CBr_4 rate-loss

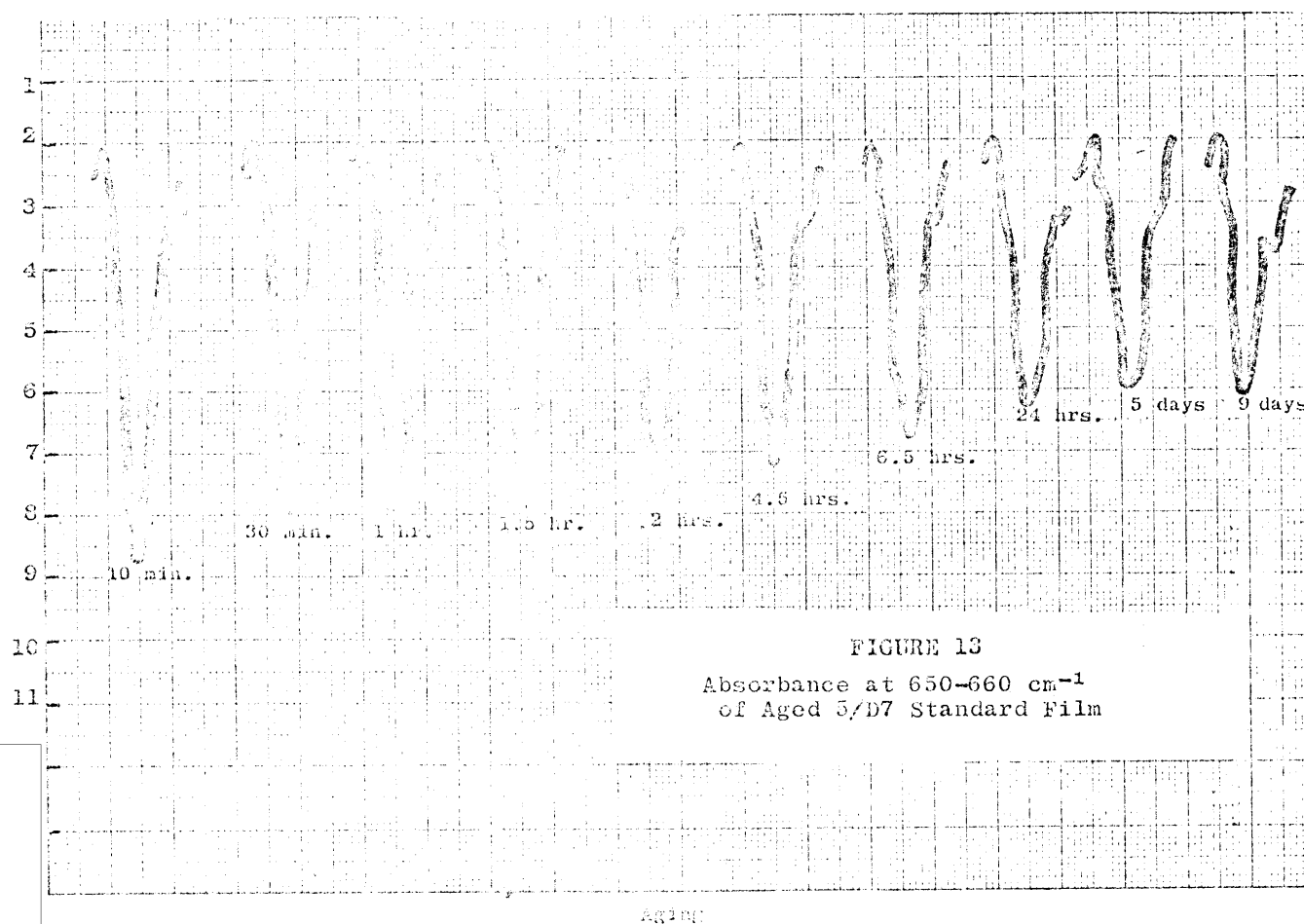
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25X1

- 24 -

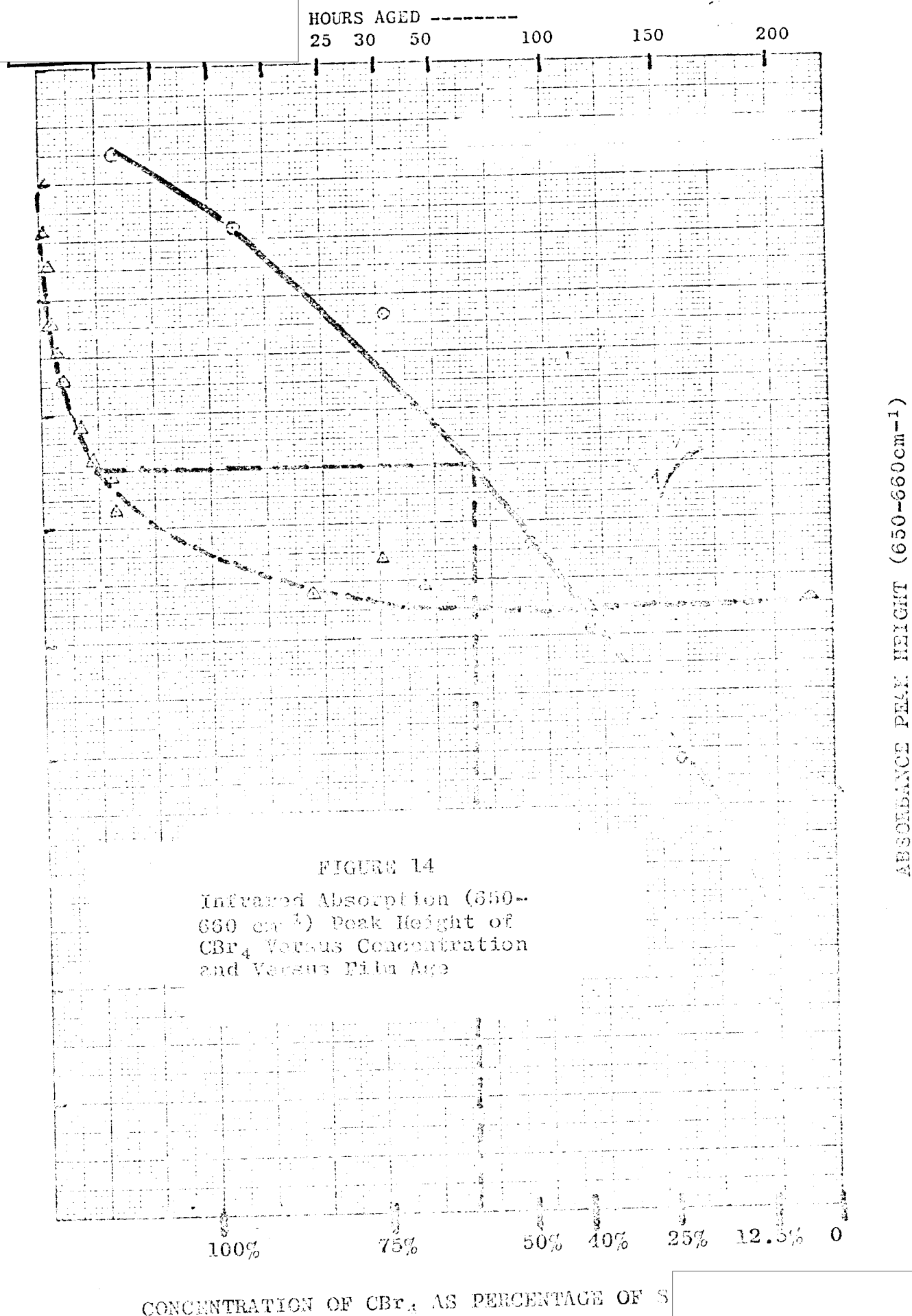
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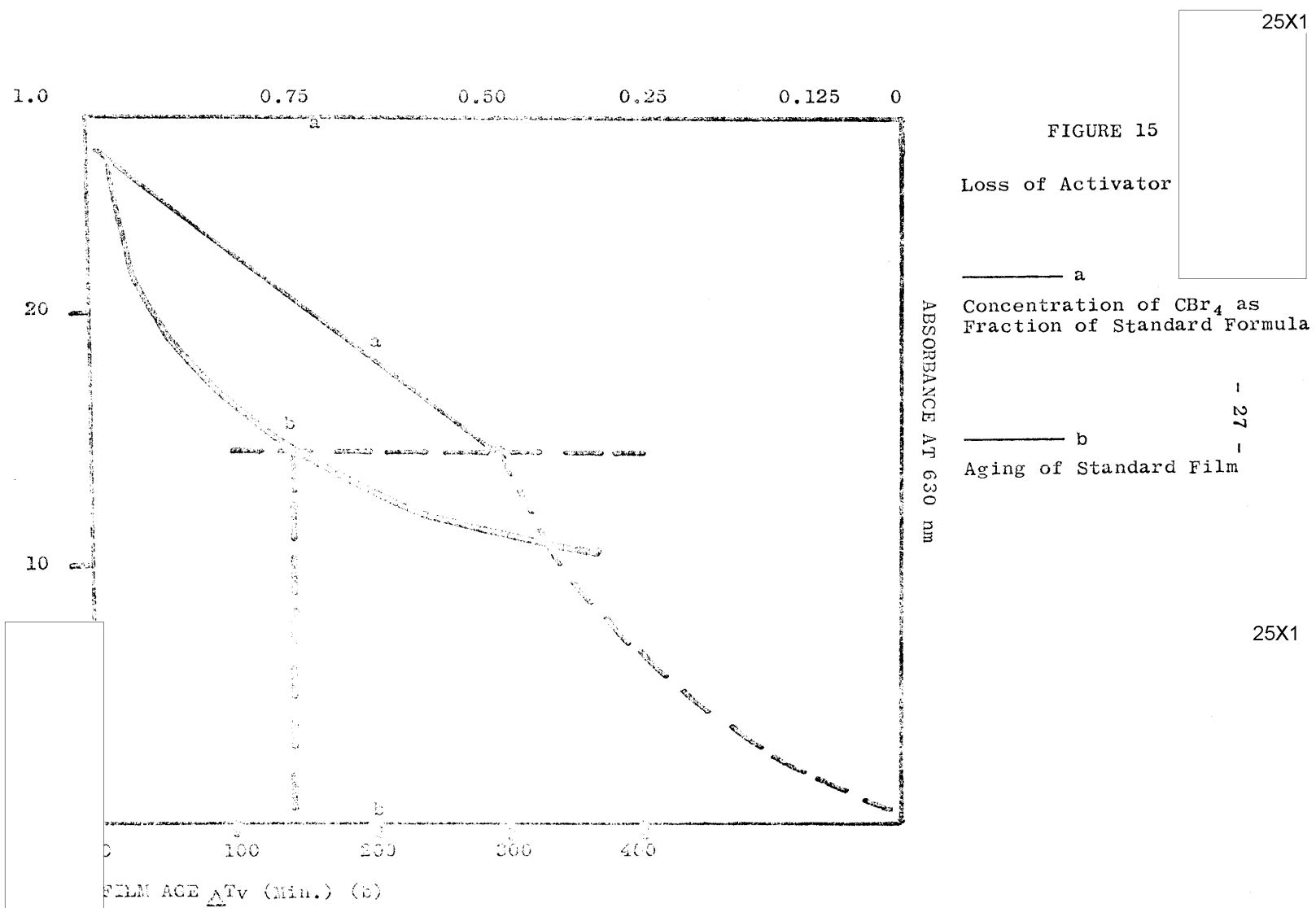


25X1

- 25 -

25X1





- 28 -

was considered inapplicable due to concurrent loss of benzene. After several weeks, however, little if any benzene should remain, while on the other hand, the CBr_4 concentration has stabilized for over a week at 40 to 50%. Two pieces of film, two weeks old, measuring approximately 31 and 18 cm^2 respectively were weighed and then heated in a forced-draft air oven at 160°C for three minutes, cooled and reweighed. The absences of infrared absorption at 650 to 660 cm^{-1} confirmed the total removal of the remaining CBr_4 . The weight losses therefore corresponded to the CBr_4 which had remained in the aged film. The original CBr_4 loading per unit area is readily computed from formulation data and known coating thickness. The weight losses corresponded to 44% and 51% CBr_4 for the two films respectively. These data are in good agreement with the infrared method (Figure 14), especially when one considers the present lack of refinement in experimental methods and data analysis.

1.1.1.3.2 Simulated Speed Decay

The primary causes of speed decay were determined during the last contract period⁴. One cause is loss of activator, a purely physical phenomenon, while another cause is chemical in nature. On the basis of circumstantial evidence the chemical cause was postulated to be formation of 4DMAP (4-dimethylamino-phenol). The 4DMAP in turn arises from decomposition of D260-hydroperoxide resulting from autoxidation of D260. The complex chemistry of the camera speed film materials raises questions about still other, as yet unrecognized, chemical causes of speed decay, and some of these possibilities have been discussed previously⁵.

The ability to independently determine the CBr_4 loss-rate, provides the means of evaluating independently the relative contributions of the two causes of speed decay, and in turn provides the means of testing the chemical speed decay hypothesis (cf. Section 1.1.1.3.2.2).

1.1.1.3.2.1 Loss of Activator (CBr_4)

The first step was to determine the speed decay due to loss of CBr_4 , independent of chemical decay. DPO and RLD D-Log E curves of fresh films, formulated with different concentrations of CBr_4 , were compared to the curves of the standard formulation. The results for 5/D7 are seen in Figures 16 and 17. Figure 16 shows fairly regular loss of sensitivity and density with decreasing

25X1

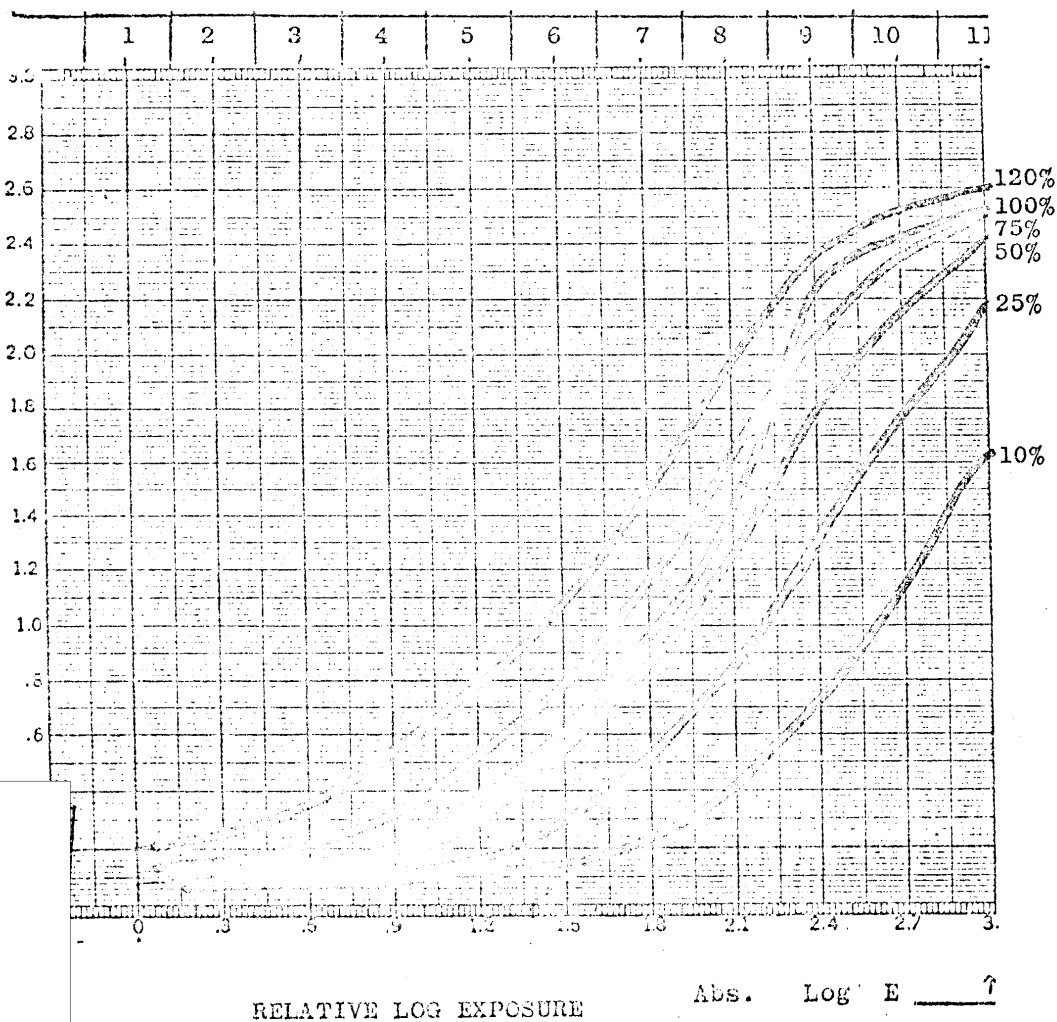


FIGURE 16

5/D7 System - CBr₄ Travel 25X1

Printout Mode
(Te = 300 sec)

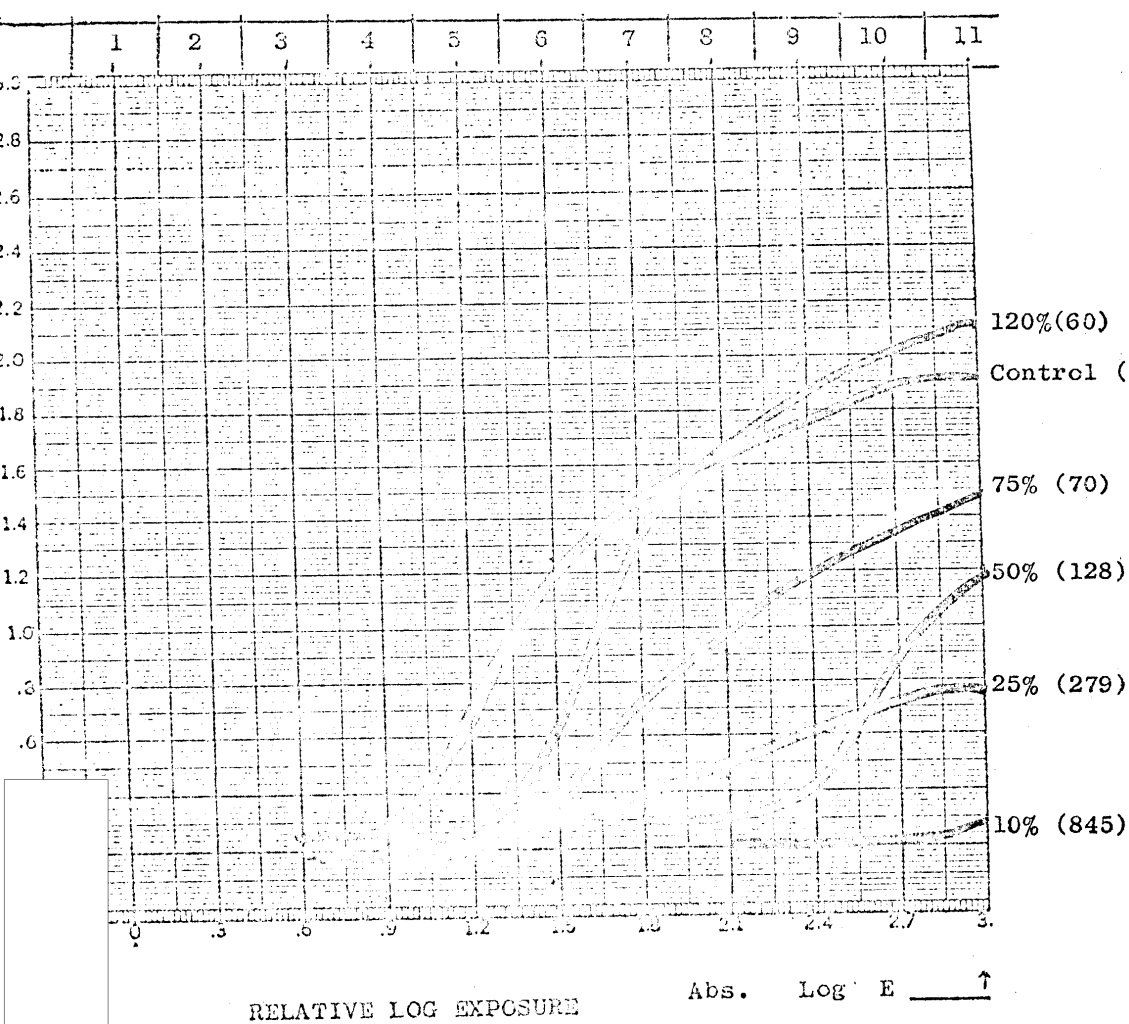


FIGURE 1

5/D7 System-CBr
RLD Mode

$T_e = .09 \text{ sec.}$
(Tr) = (Sec.)

25X1

rsal

- 30 -

25X1

- 31 -

concentration of CBr_4 (the curves are denoted as percent CBr_4 relative to 100% for the standard formulation). The effect of concentration is far more dramatic (Figure 17) in the RLD mode. Undue emphasis should not be placed on discrepancies in the apparent trend of curve shapes since many other parameters can affect shape. The overall trend of lower speed, lower density and longer development times is unmistakable nevertheless. Analogous behavior occurs with the 5/D8 system (Figures 18 and 19).

This greater effect of CBr_4 -concentration on the RLD mode explains, at least in part, the previously noted fact⁶ that speed decay appears more rapid in this mode than in the DPO mode.

Nevertheless, loss of CBr_4 is not the sole cause of speed decay. This becomes readily apparent when these D-Log E curves are compared to those describing the speed decay of film (Figures 20 and 21). In the DPO mode of 5/D7 (Figure 20) the D-Log E curve for a 1 hour old film corresponds to a fresh film containing about 25% CBr_4 (Figure 16). Yet the loss of CBr_4 never exceeds about 60% which corresponds to an equilibrium loading of 40% (Section 1.1.1.3.1, Figure 14). This fact is even more dramatic in the RLD mode (compare Figure 21 with 17), especially when a 5 second latent image exposure was required for decayed film, compared to a 1/8 second exposure for fresh films. Comparable behavior was exhibited by 5/D8 (Figures 22 and 23).

The differences between actual speed decay and speed decay simulated by altering the concentration of CBr_4 must be attributed to still another cause, presumably the chemical decay.

1.1.1.3.2.2 Chemical Decay

Attempts were made to simulate the speed decay of 5/D7 film by combining the addition of 4DMP with loss of CBr_4 . If the postulated formation of 4DMP is the sole chemical decay factor then proper combination of these two parameters in fresh film should simulate actually decayed films. This assumption is naive since it neglects possible secondary reactions of 4DMP that might be occurring during actual decay and it neglects the simultaneous formation of D260-anthrone. Although failure to simulate decay would not prove therefore that chemical decay mechanisms other than the one postulated are occurring, successful simulation would provide assurance that only the postulated chemical

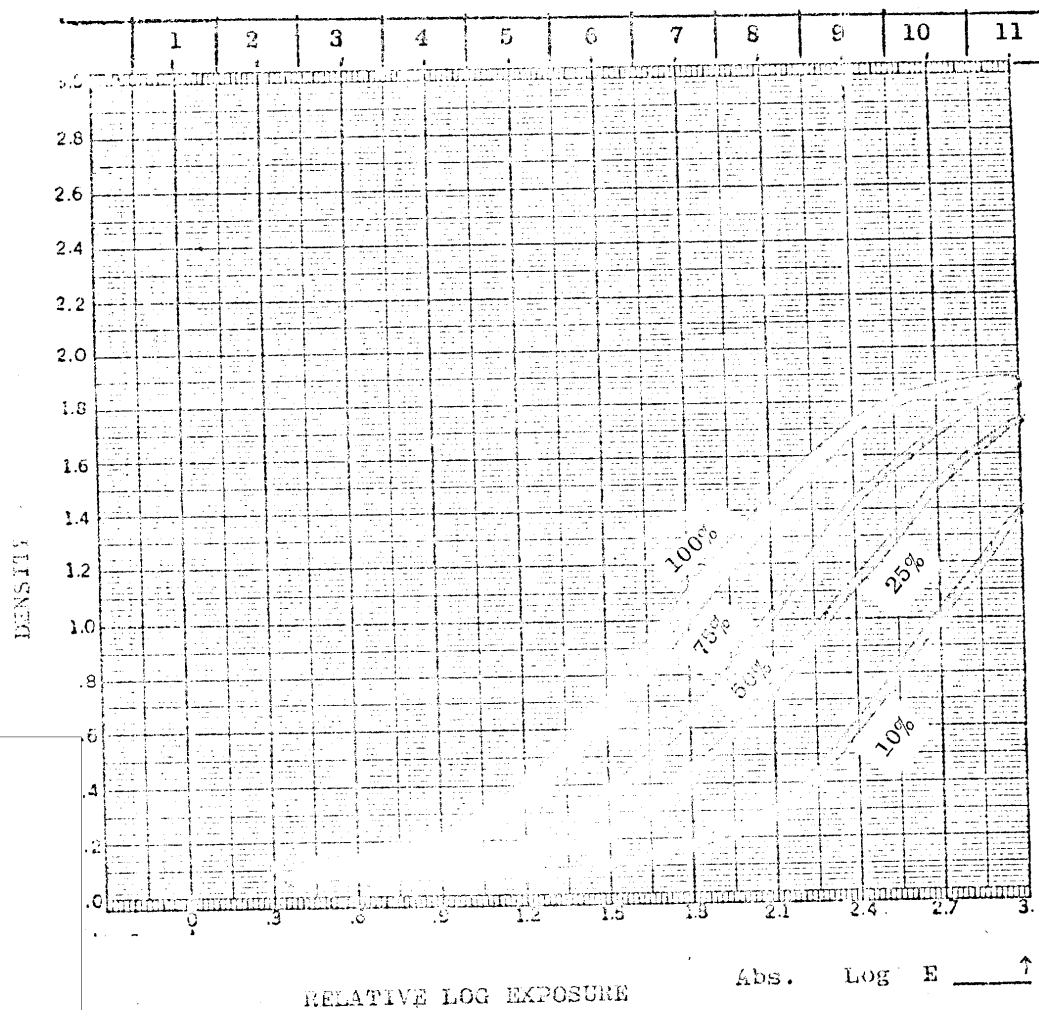


FIGURE 18
CBr₄ Traversa
Formula 5/D8
Direct Printout
(Te = 300 se

25X1

- 32 -

25X1

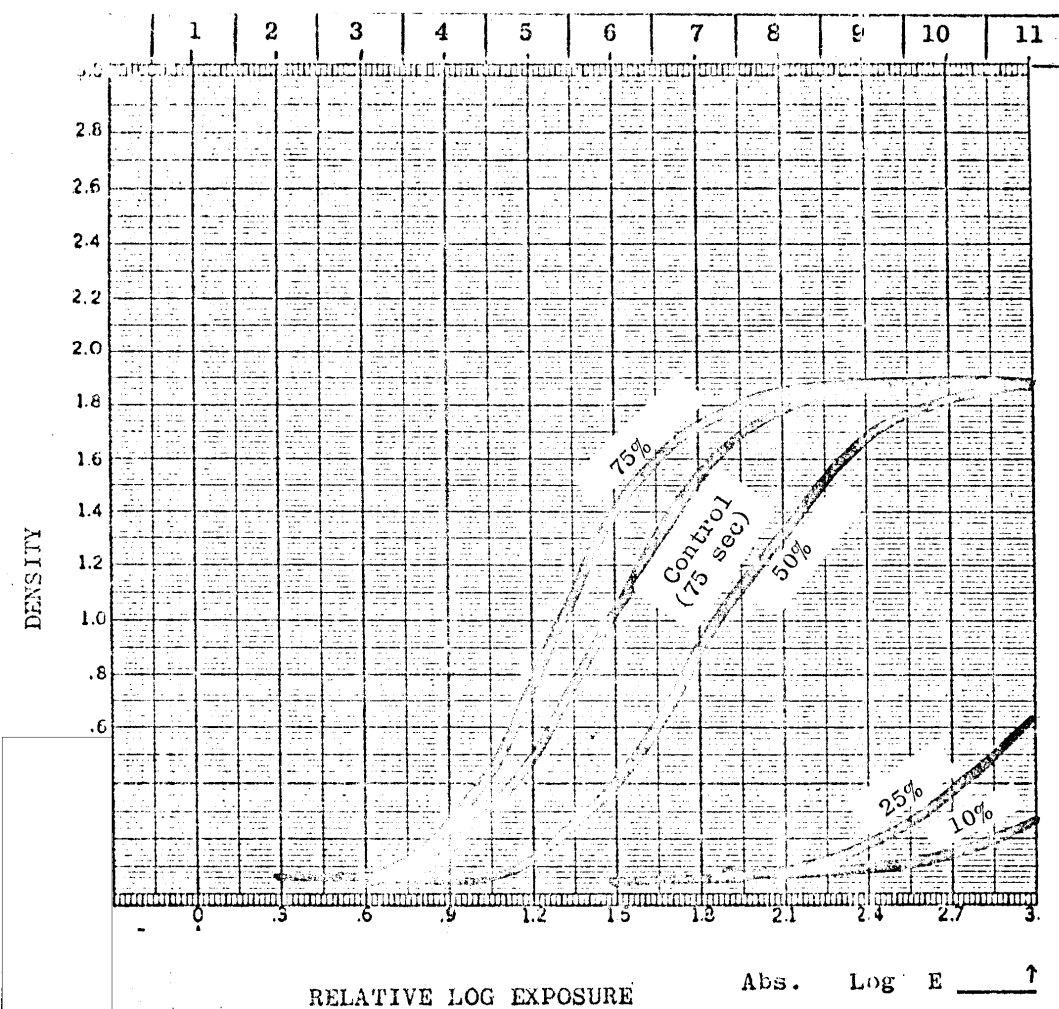


FIGURE 19
CBr₄ Travers
Formula 5/D8
Red Lite Devel
(Te = 5 sec; Tr

25X1

c)

- 33 -

25X1

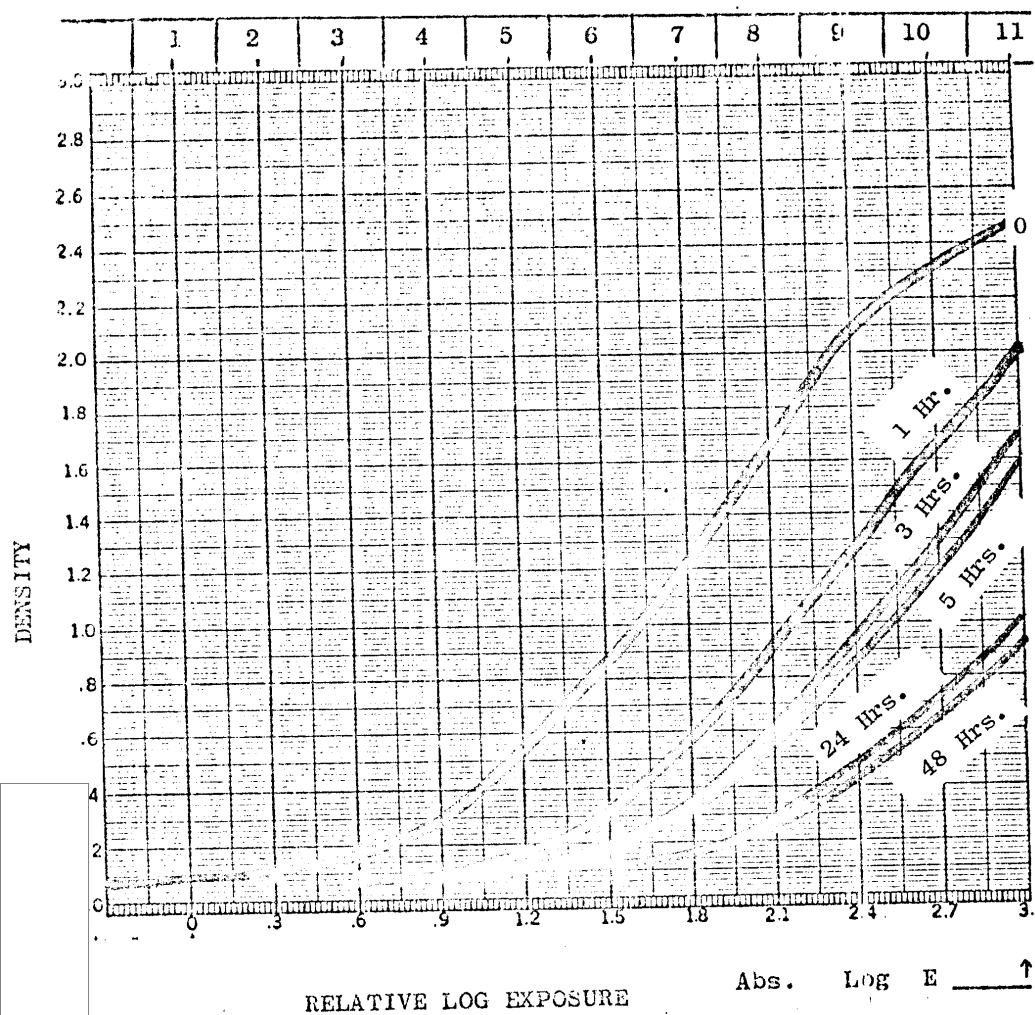


FIGURE 20
5/D7 Control: Aging
Direct Printout
($T_e = 300$ sec.)
64 mg D7

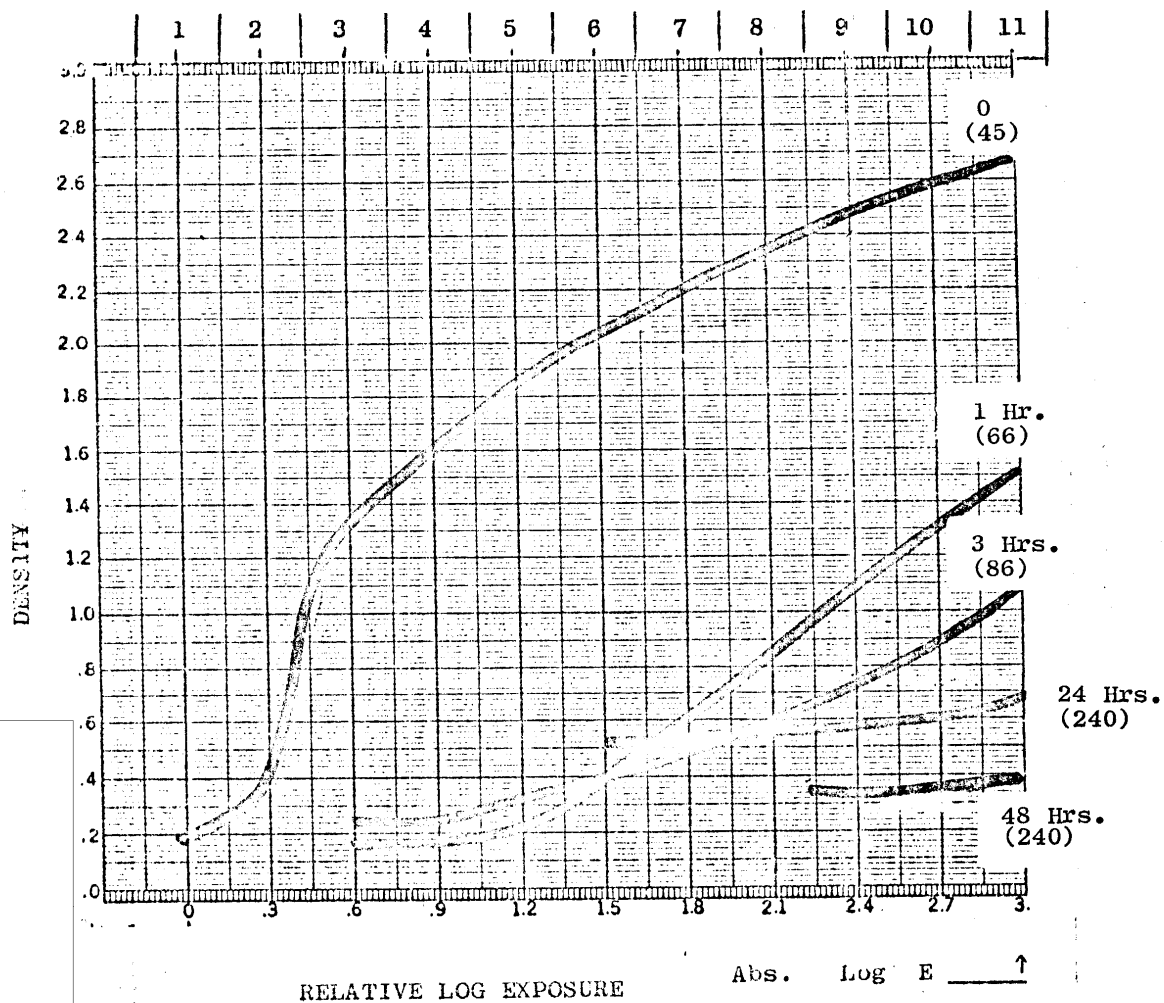


FIGURE 21
5/D7 Control: A
Red Lite Develo
(Te = 5 sec.
64 mg D7

25X1

- 35 -

25X1

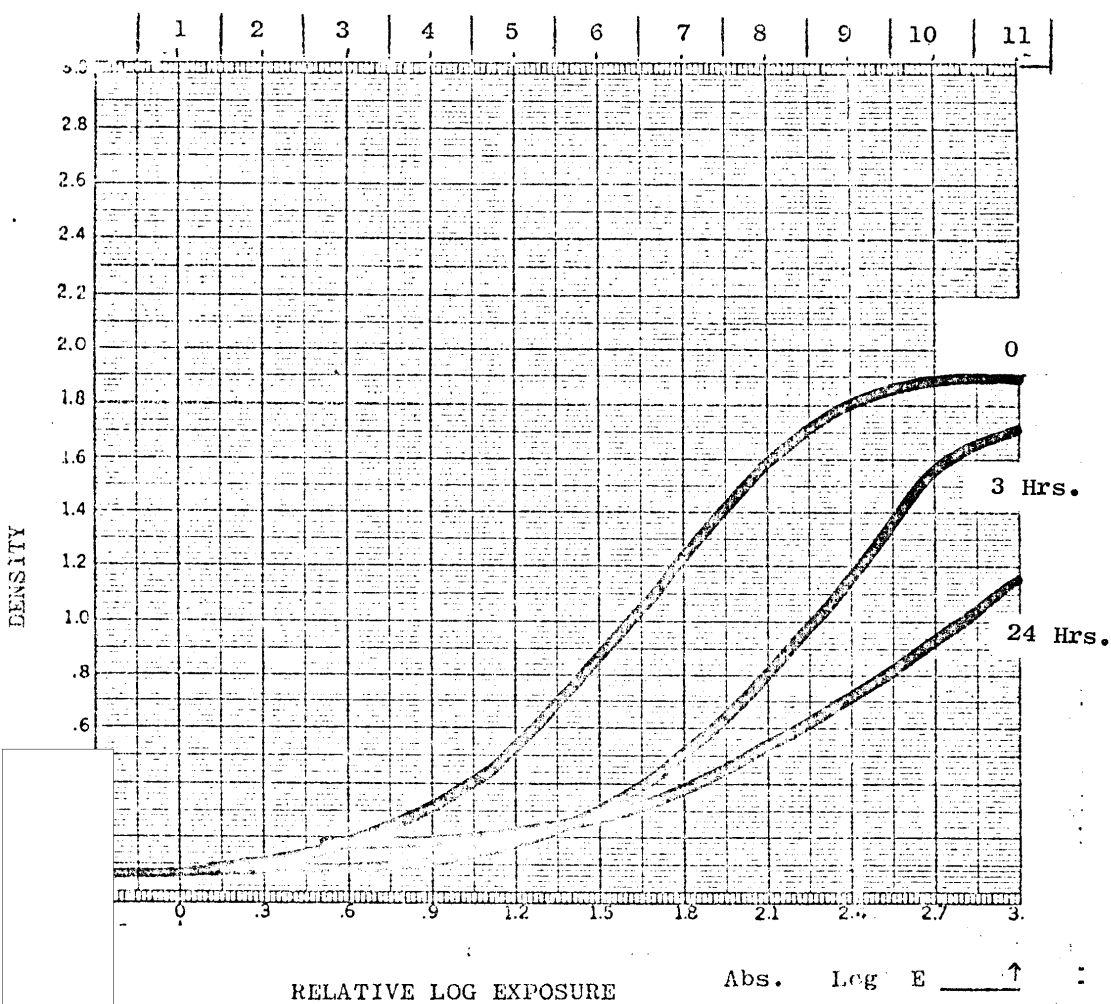


FIGURE 22
5/D8 Aging Study
Direct Printout
(Te = 300 sec.)
40 mg D8

25X1

- 36 -

25X1

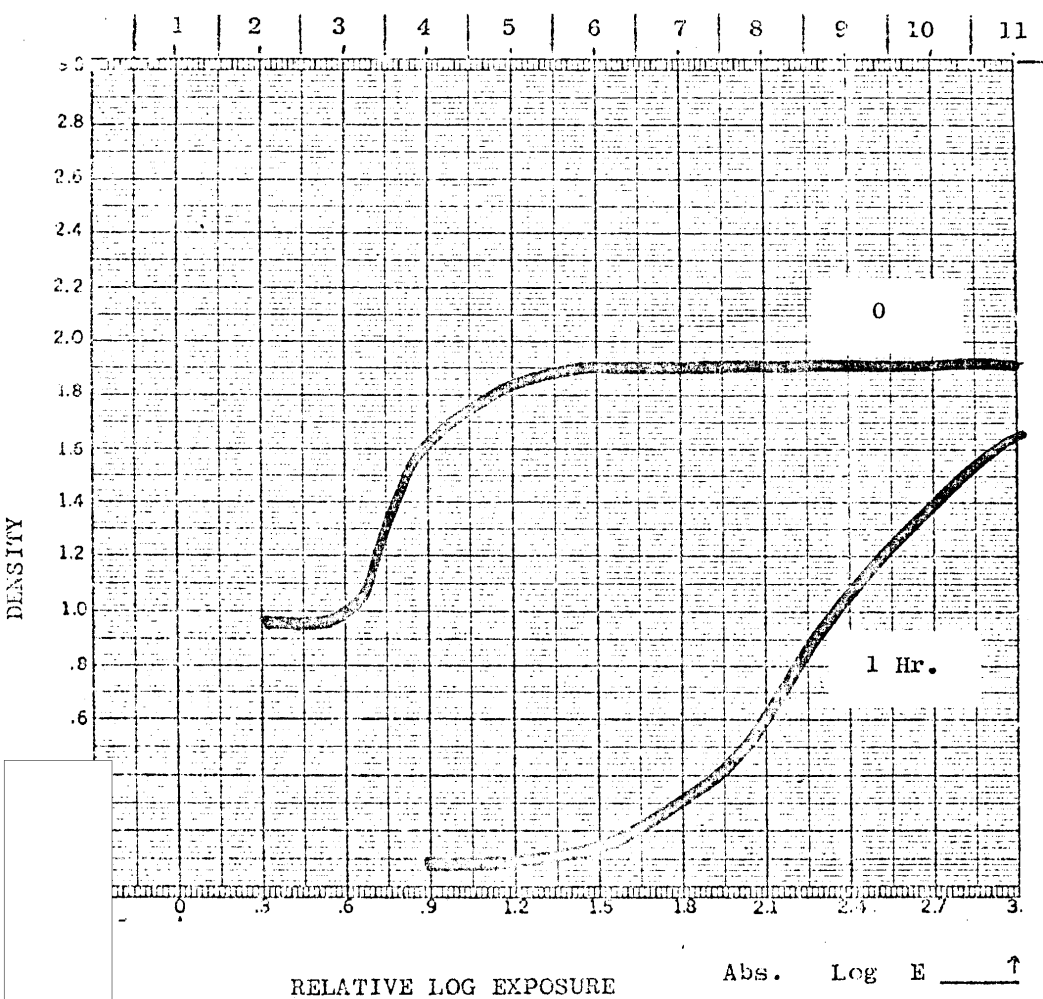


FIGURE 23
5/D8 Aging Study
Red Lite Development
(Te = 5 sec.)
40 mg D8

25X1

- 37 -

25X1

- 38 -

decay mechanism is occurring. Furthermore, successful simulation over a range of decay times would provide (by the known amounts of 4DMAP added) a rate for the chemical decay.

The first step was to simulate observed DPO decay (Figure 20) for any given time by adding 4DMAP to fresh films containing the concentration of CBr_4 indicated for that time by the known loss-rate (Figure 14, page 26). A previous traversal of 4DMAP in 5/D7 (Figure 24) provided the necessary ranges of 4DMAP to be traversed for each age period.

The study began by attempting simulation of a one hour aged film (see Figure 20). The measured CBr_4 loss-rate (Figure 14) indicated that as much as 30% CBr_4 was lost during the first hour; consequently, the traversal of 4DMAP was evaluated with fresh film formulated with 70% CBr_4 . Results are seen in Figure 25 and show that 2.5 to 5.0 μg of 4DMAP closely approximates a one hour decay (compare with Figure 20). Before attempting to fine-tune the simulation, a check was made on the RLD mode (Figure 26) and the results were in no way comparable to decayed film (Figure 21). Obviously, more formation and presence of 4DMAP is not the sole cause of chemical speed decay. This conclusion is supported by the inability to detect the formation of 4DMAP in the presence of 4PO and/or D7 (cf. Section 1.1.5.2).

The D260-anthrone, D427, is formed simultaneously with 4DMAP (Scheme 1) and although additions of anthrone to 5/D7 have no effect the simultaneous presence of both could be necessary for the manifestation of chemical decay. The preceding simulations were repeated in both DPO and RLD modes, this time with equimolar amounts of both 4DMAP and D260 anthrone. The results were identical, proving the nonexistence of synergism between these two decay products.

4DMAP is readily oxidized as evidenced by its fairly rapid discoloration (several hours). In fact its desensitizing effect on films is attributed to its ease of oxidation; in other words, it is a good reducing agent. It is reasonable to expect that 4DMAP formed during chemical decay is further transformed by interaction with oxygen or other film ingredients, and that one or more of these transformation products may be the direct cause of chemical speed decay. On the other hand, failure to simulate decay may be due to still other chemical mechanisms. That other mechanisms are operating should be expected since autoxidation is a free-radical reaction and the film ingredients other than D260 are also susceptible to free-radical reactions. If this is the case, inhibition of autoxidation, which is the

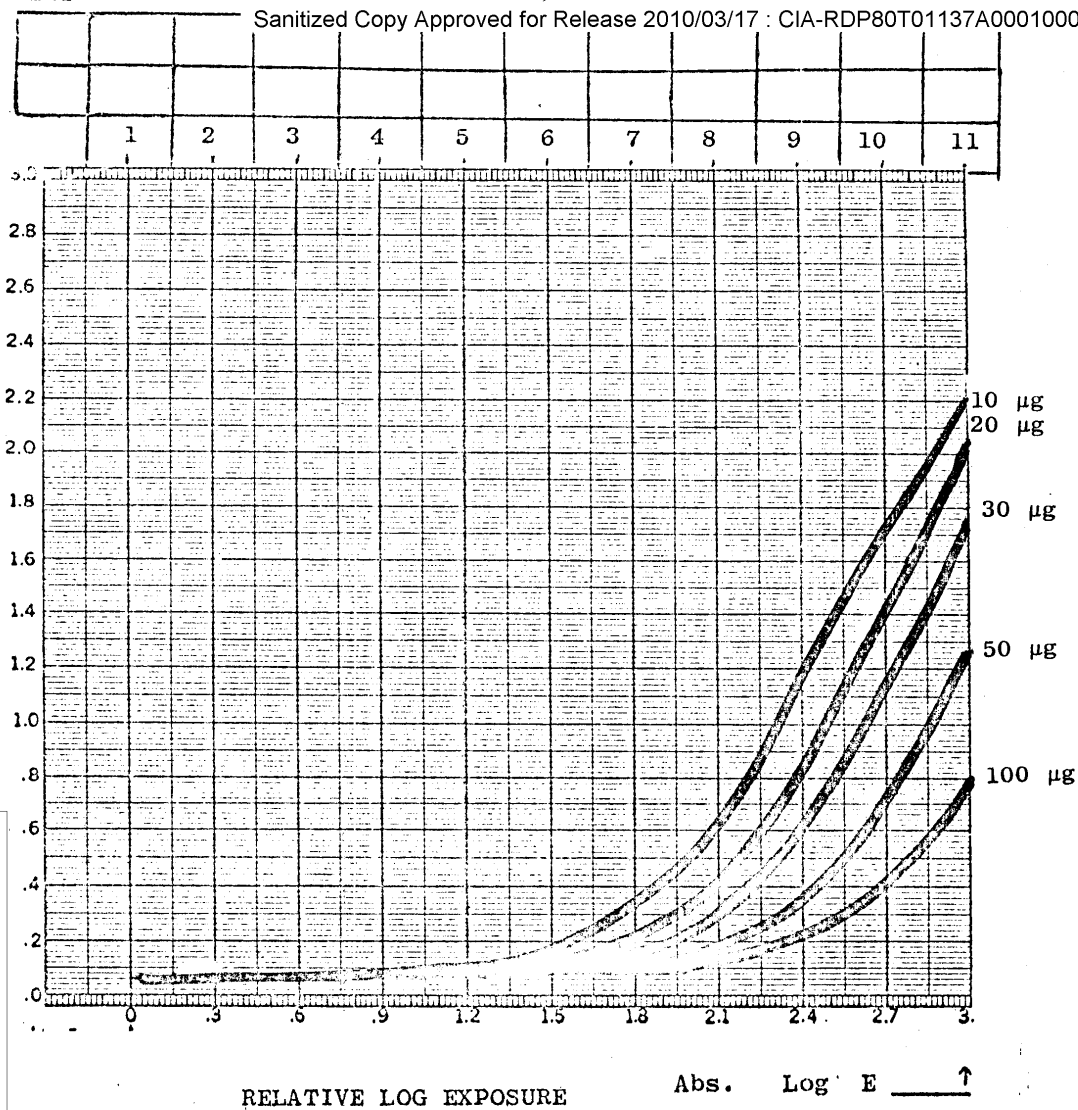


FIGURE 24
5/D7 - 4DMPA
DPO
(Te = 300 s)

25X1

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25X1

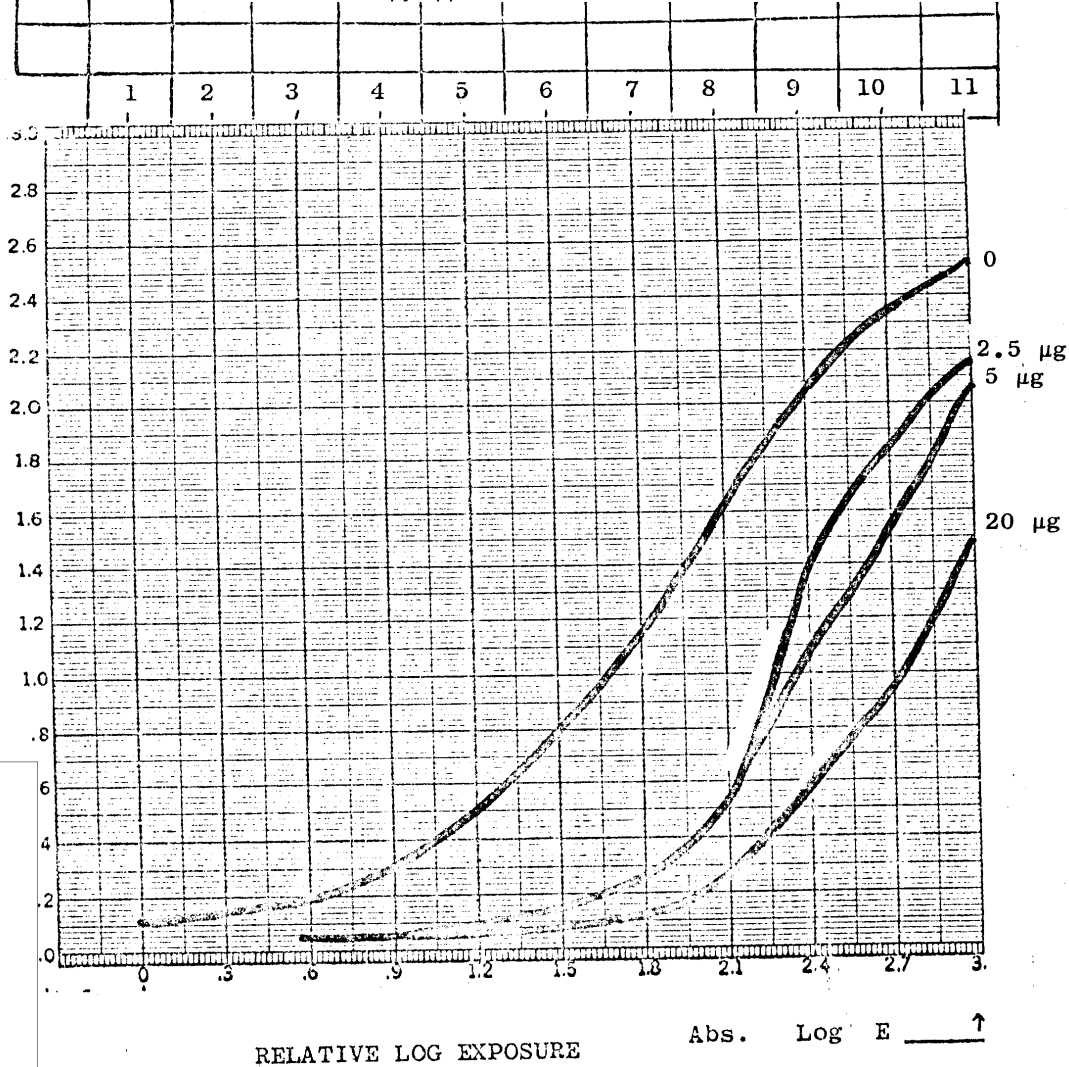


FIGURE 2 25X1

5/D7, 70% CBr
4DMAP Additive

DPO
(Te = 300 s)

- 40 -

25X1

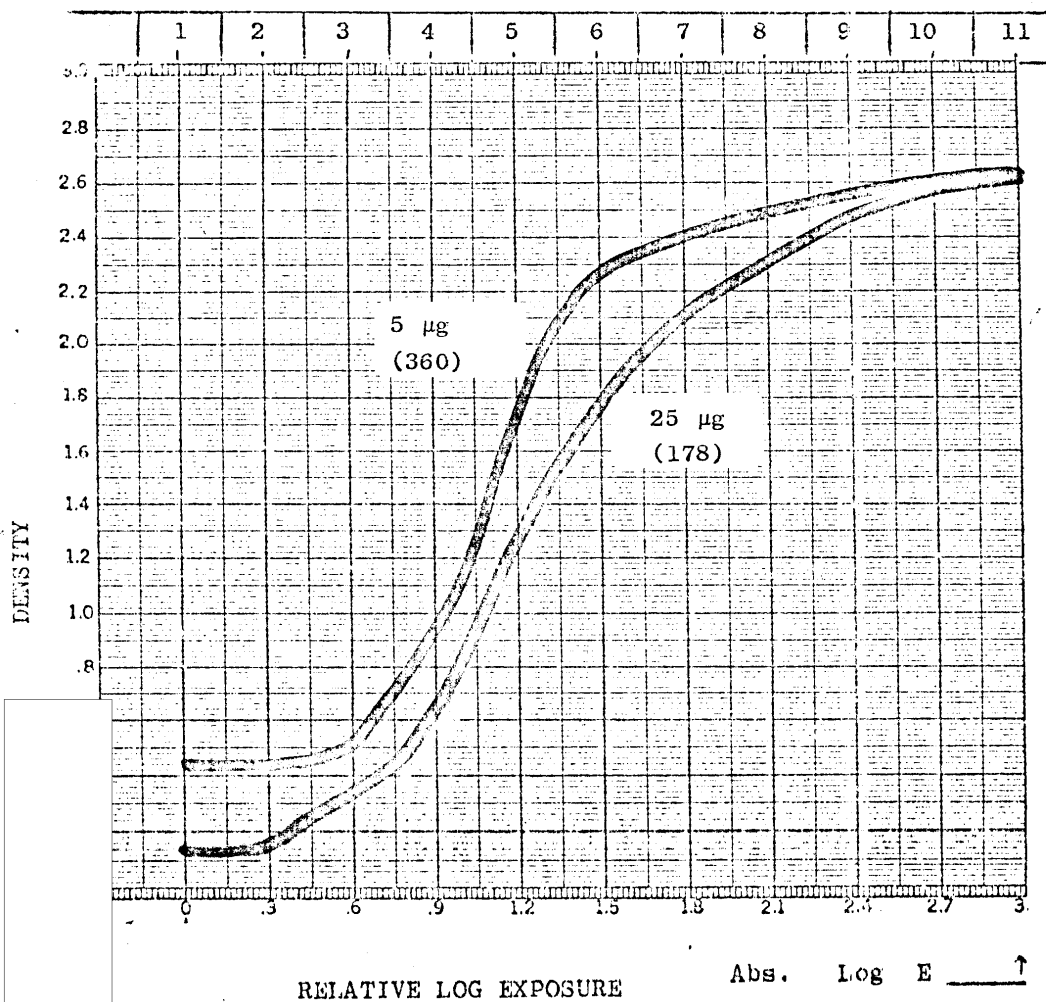


FIGURE 26
5/D7, 70% CBr_4
4DMAP Addition
RLD
($T_e = 5 \text{ sec}$)

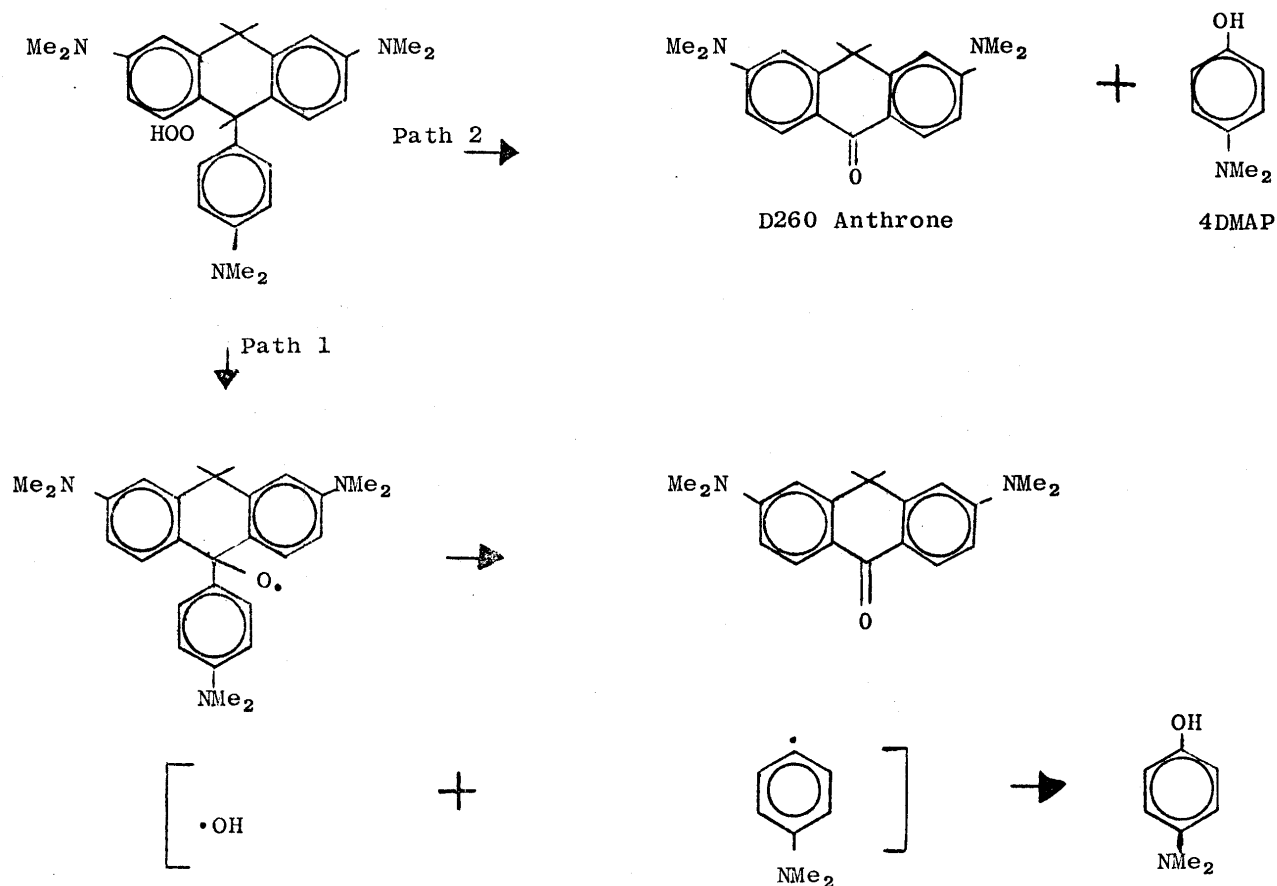
25X1

- 41 -

25X1

SCHEME 1

D260-HYDROPEROXIDE DECOMPOSITION AND REARRANGEMENT



25X1

- 42 -

25X1

- 43 -

main approach to arresting chemical speed decay, will be effective whether the postulated formation of 4DMP is the sole cause or not.

For a discussion of other phenolic products which are probably formed concomitant with 4DMP, see Section 1.1.3.3.

1.1.1.3.3 Ingredient Interaction Decay Studies - Formula 5/D8

Stock solutions of D260 and D8 with and without 4PO were allowed to age 20 days both in air and in argon. The solutions were initially made in an argon atmosphere using de-oxygenated ingredients. A portion of each solution was transferred to a chamber containing synthetic air (80% N₂, 20% O₂) and shaken periodically to assure displacement of the argon. Films were run periodically with the remaining ingredients added just prior to coating.

Changes in the DPO made are seen in Figures 27 and 28. Note that after 20 days there is no change in the absence of oxygen as compared to a significant drop in sensitivity in the presence of oxygen. Note also the moderating effect of 4PO. This behavior in argon parallels the behavior of D260 (Figure 29) and D260/4PO (Figure 30) which were done earlier as part of the 5/D7 interaction studies. Unfortunately, the earlier studies with 5/D7 in air did not include the printout mode. In contrast to this behavior, D260/D7 (Figure 31) and D260/D7/4PO (Figure 32) showed some decay in the absence of oxygen. In this instance 4PO appeared to have a detrimental rather than moderating effect, but this is probably not real since 4PO has already been shown to moderate speed decay in this system.

The RLD mode shows more strikingly the effects of air and 4PO on the aging of D260/D8 (Figure 33) and D260/D8/4PO (Figure 34). In the absence of 4PO, air causes dramatic loss of sensitivity with a six-fold increase in development time. In the presence of 4PO poor imaging is possible but still with a significant increase in development time. This behavior parallels that of D260 (Figure 35) and D260/4PO (Figure 36). D260/4PO/D7 also showed comparable behavior (Figure 37), but here again D260/D7 showed a striking contrast particularly in the presence of air (Figure 38).

Results from the latest 5/D8 studies concur with the conclusions drawn from the earlier studies with the 5 and 5/D7 systems. These conclusions were:

25X1

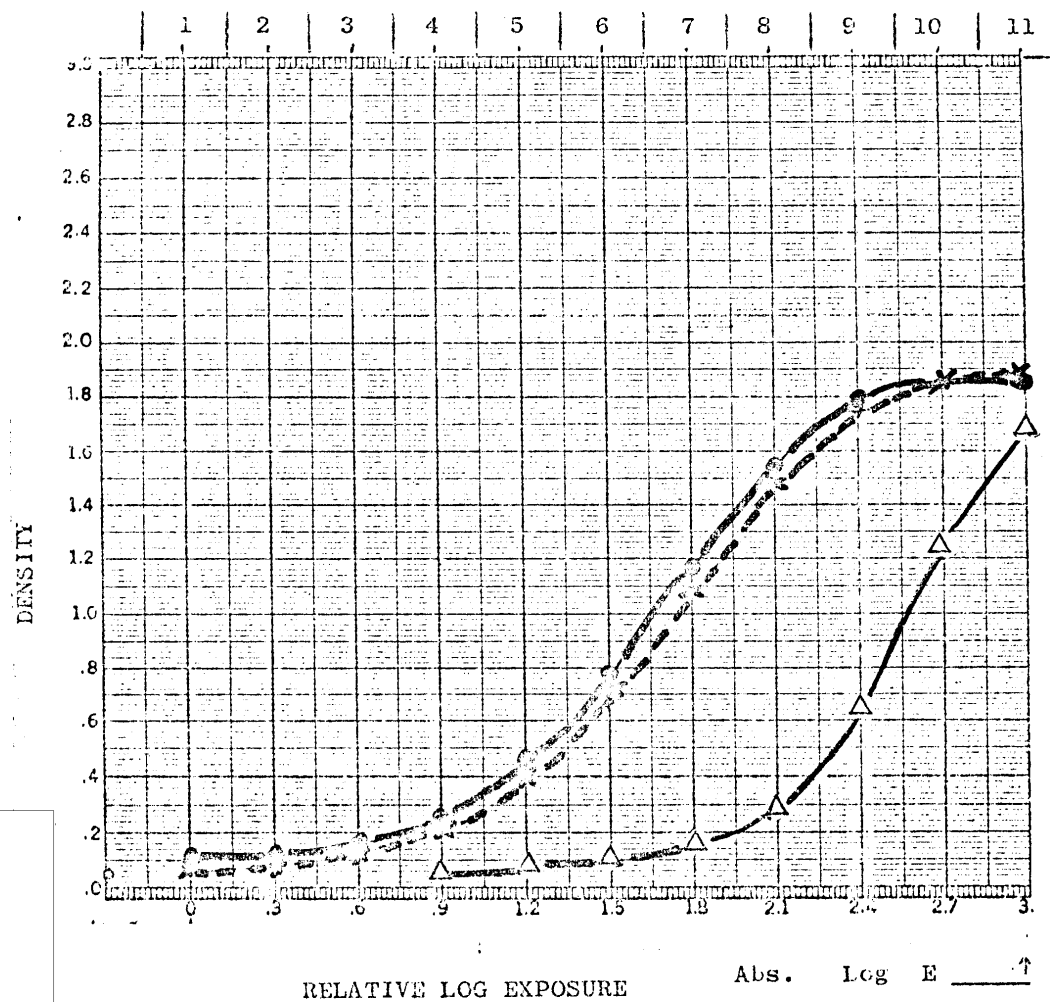


FIGURE 27

Ingredient Inte
Decay Study:
5/D8 System
D260/D8/PS
DPO Mode

Legend

- Control
- - - x - - - 20 days in argon
- △— 20 days in air

25X1

25X1

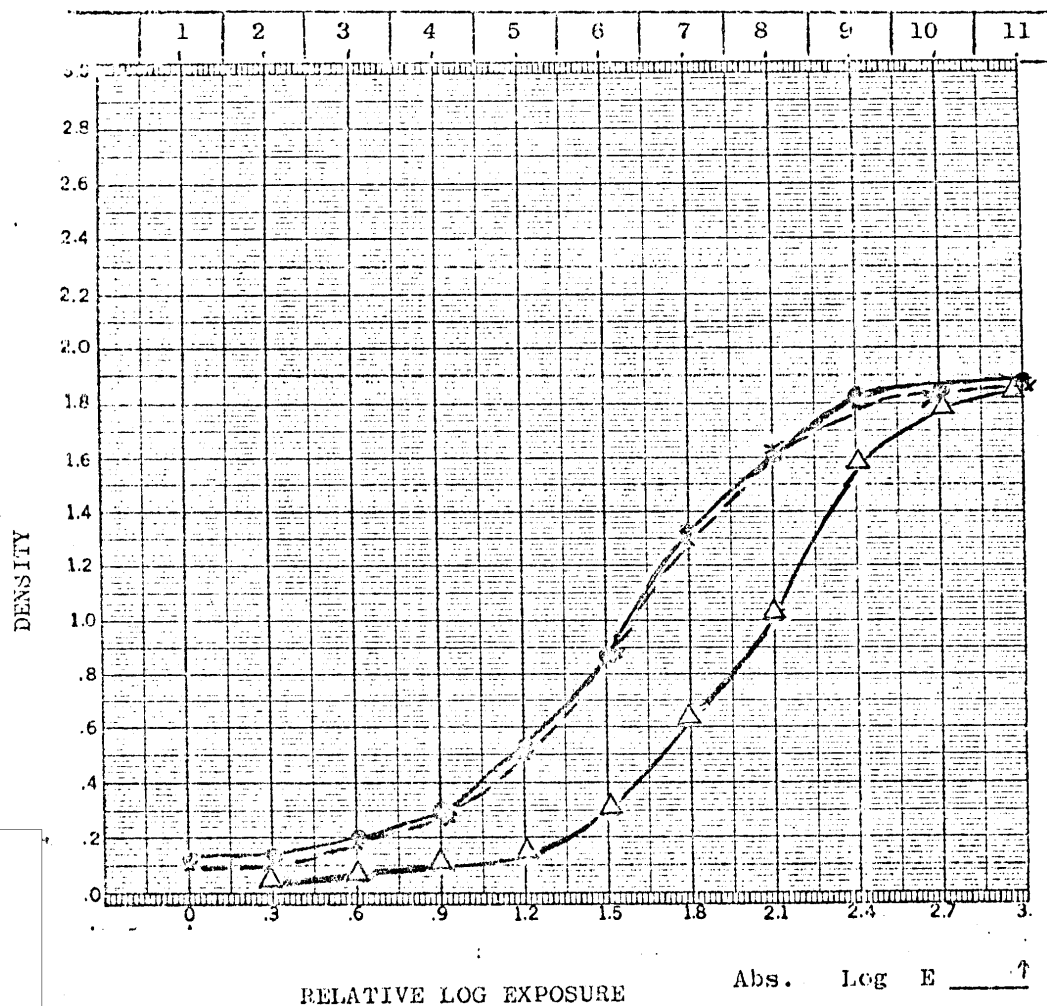
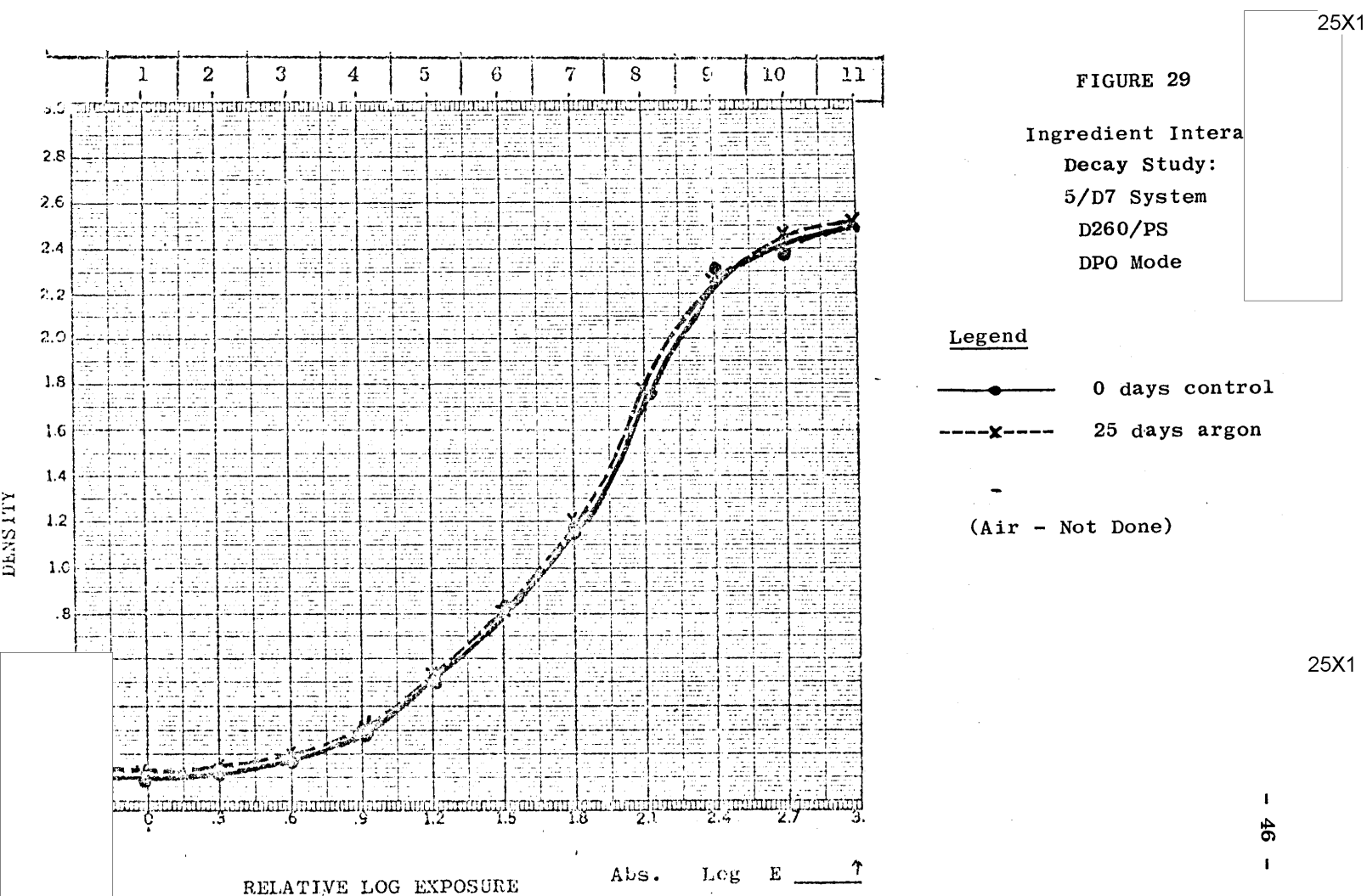


FIGURE 28
Ingredient Int
Decay Study
5/D8 System
D260/D8/4PO/E
DPO Mode

Legend

- 0 days
- - - x - - 20 days in argon
- △— 20 days in air

25X1



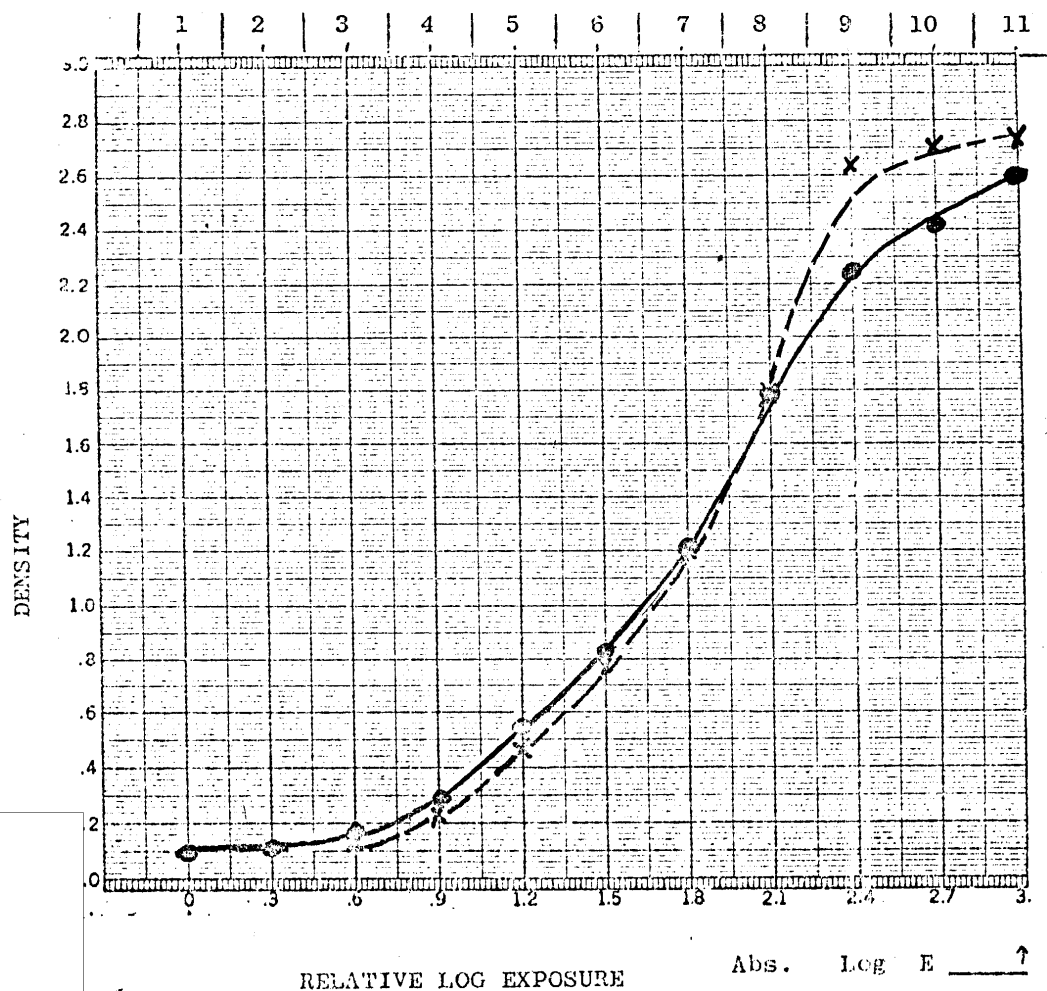


FIGURE 30

Ingredient Interaction
Decay Study:
5/D7 System
D260/4PO/PS
DPO Mode

Legend

- 0 days, Control
- - -x- - 25 days argon

(Air - Not Done)

25X1

25X1

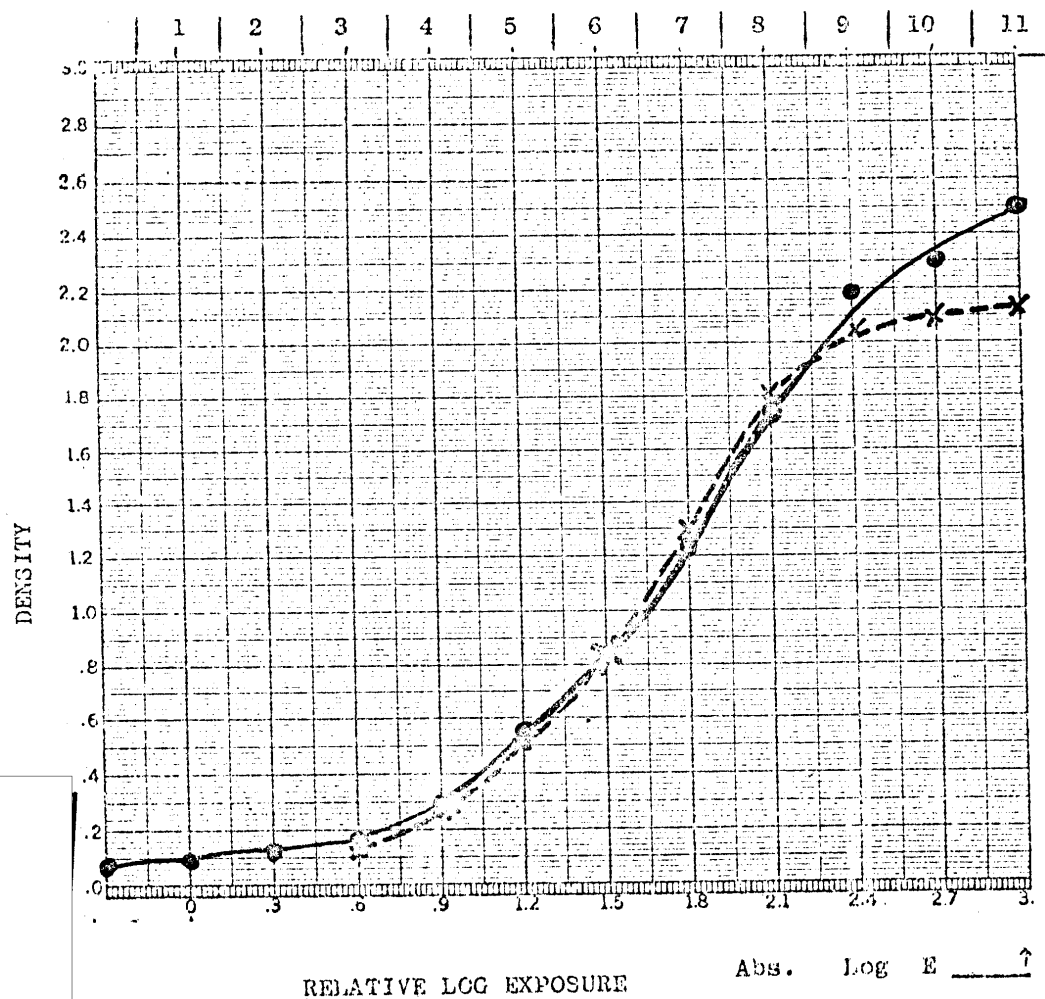


FIGURE 31

Ingredient Int
Decay Stud
5/D7 Study
D260/D7/PS
DPO Mode

Legend

—●— 0 days, Control
- - - x - - - 25 days - argon
(Air: Not Done)

25X1

25X1

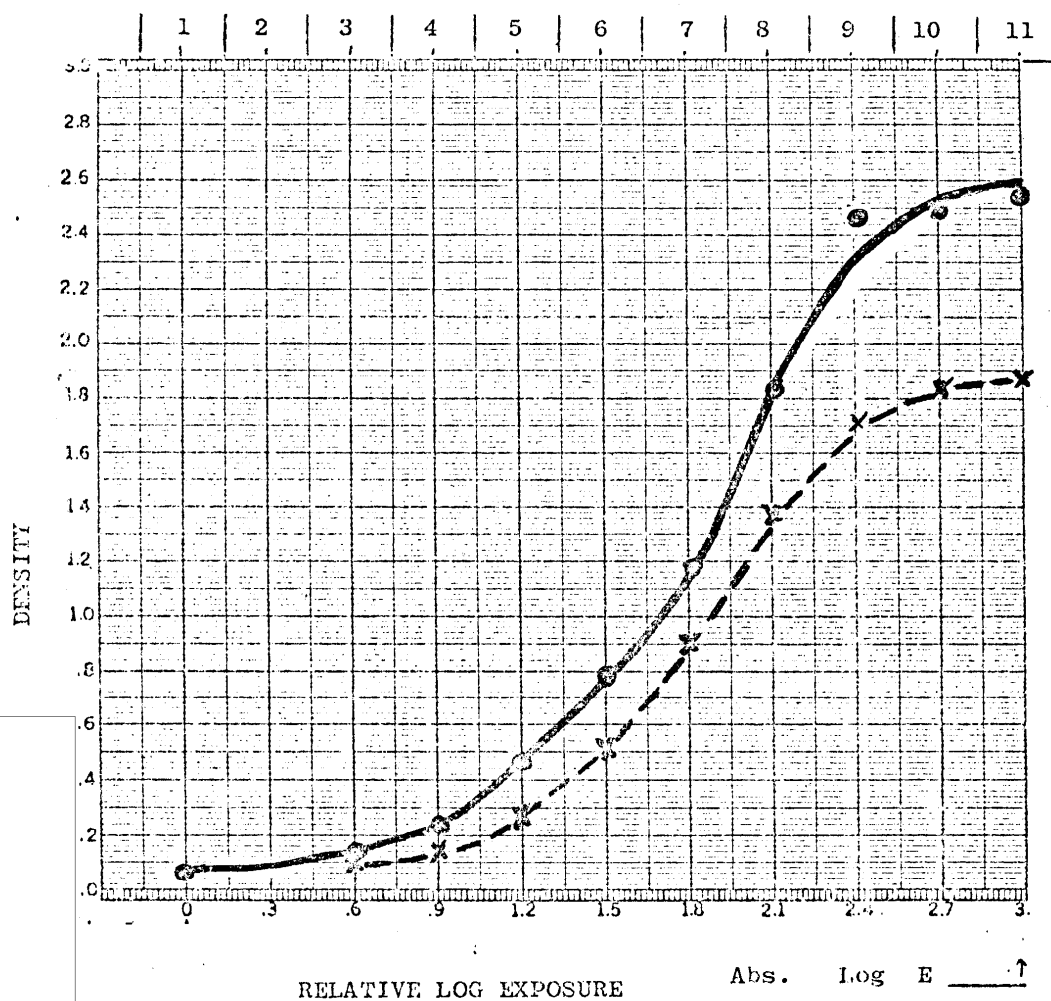


FIGURE 32
 Ingredient Inter:
 Decay Study:
 5/D7 System
 D260/D7/4PO/PS
 DPO Mode

Legend
 —●— 0 days, Control
 - - - x - - - 25 days - argon

(Air: Not Done)

25X1

25X1

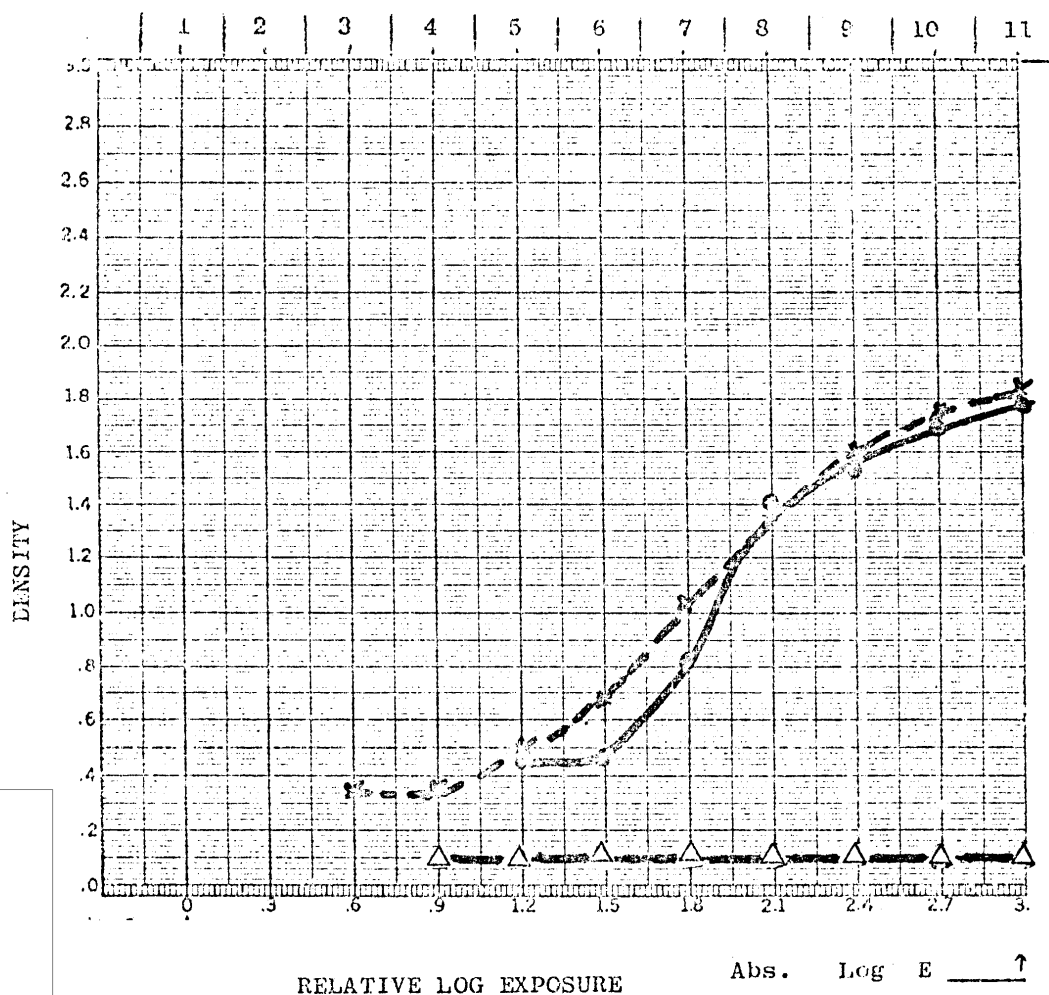


FIGURE 33
Ingredient Interaction
Decay Study
5/D8 System
D260/D8/PS
RLD Mode

Legend

- 0 days (120)
 - x--- 20 days in argon (105)
 - △— 20 days in air (720)
- (Tr in seconds)

25X1

25X1

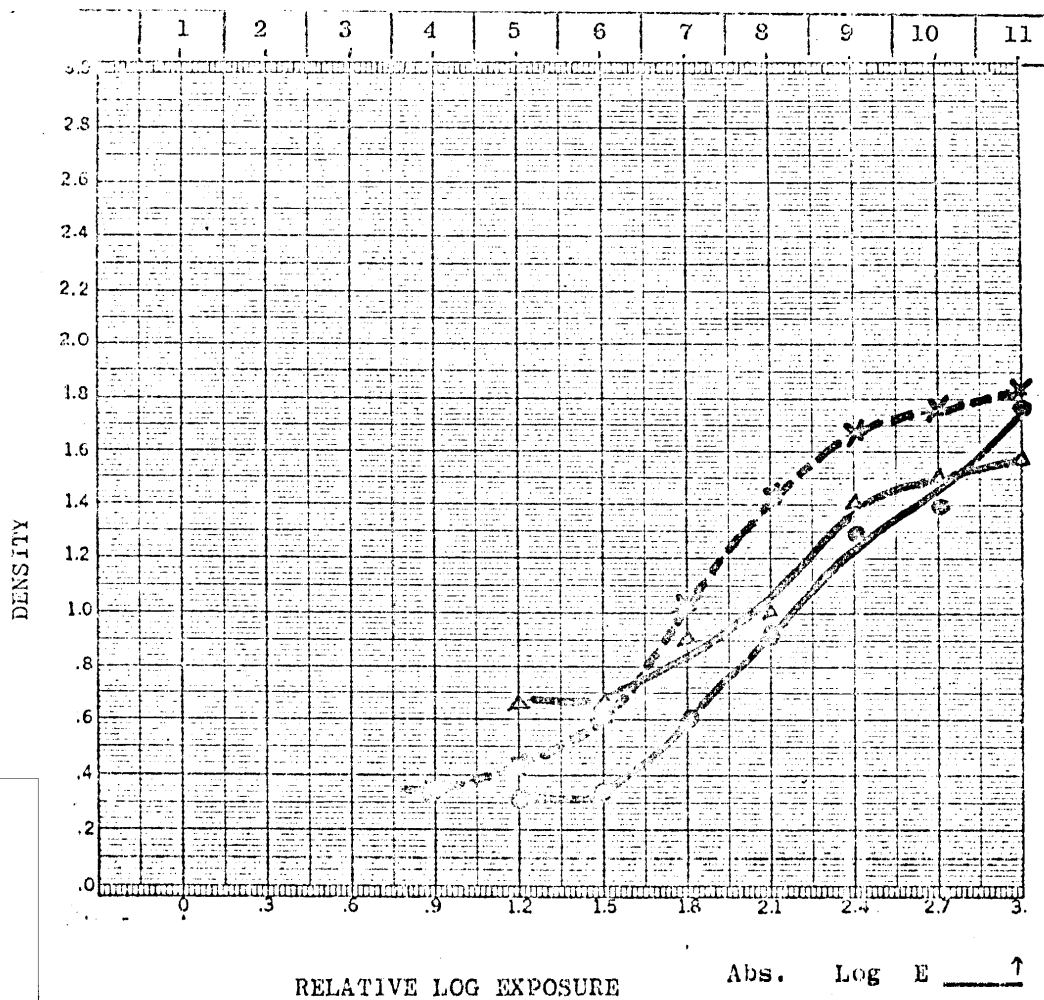


FIGURE 34
Ingredient Inter
Decay Study
5/D8 System
D260/D8/4PO/PS
RLD Mode

Legend

- 0 days (94)
 - - - x - - - 20 days in argon (87)
 - △— 20 days in air (336)
- (Tr in seconds)

25X1

25X1

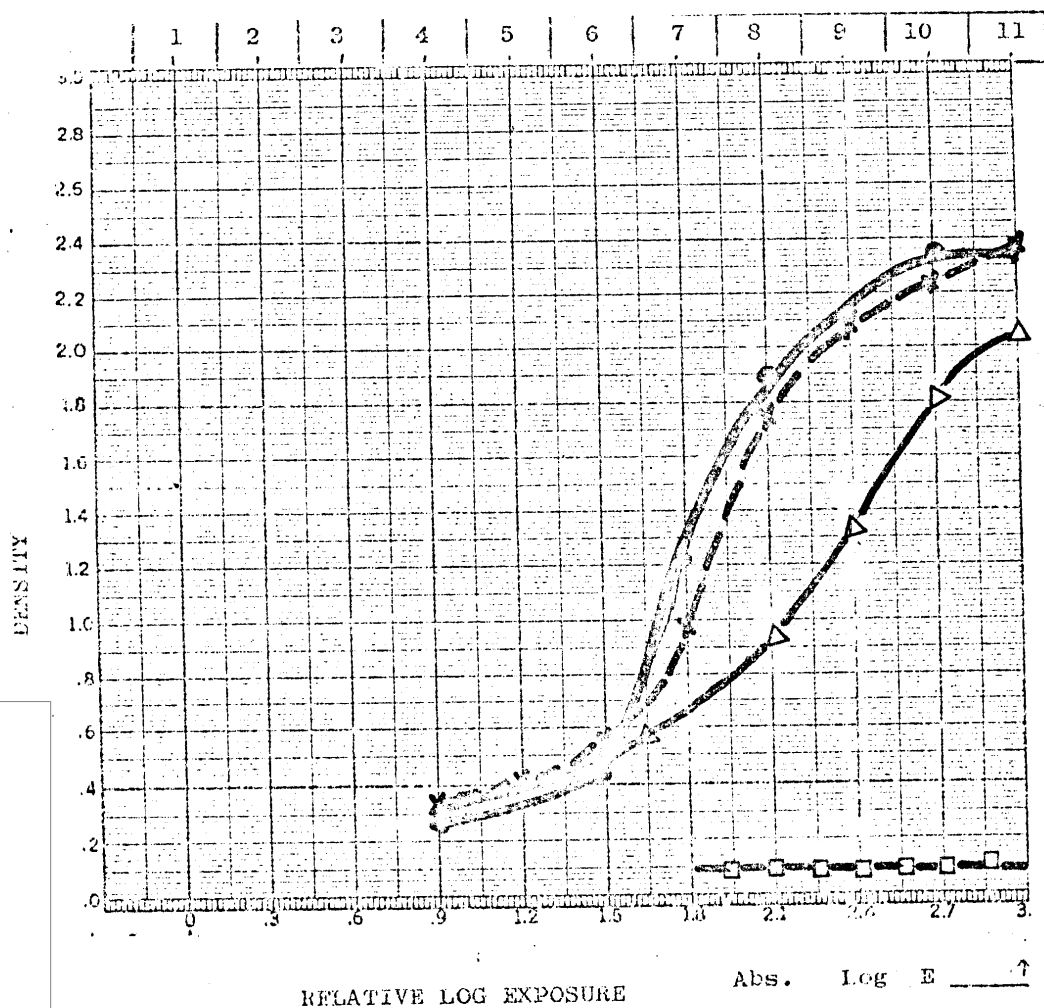


FIGURE 35
Ingredient Interaction
Decay Study
5/D7 System
D260/PS
RLD Mode

Legend

- 0 days, Control (31)
- x--- 25 days argon (81)
- △— 20 days air (246)
- 38 days argon (300)
- 34 days air

(Tr in seconds)

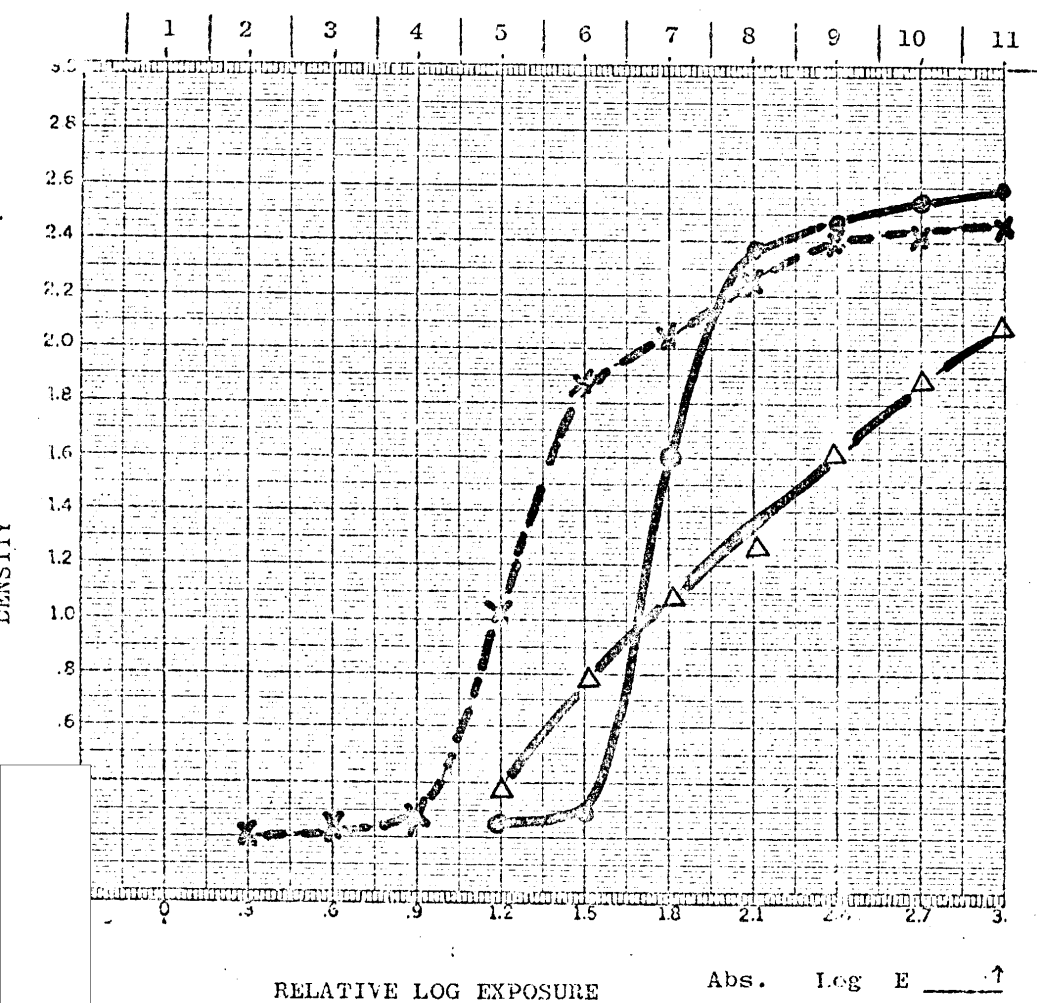


FIGURE 36
Ingredient Interaction
Decay Study:
5/D7 System
D260/4PO/PS
RLD Mode

Legend

- 0 days, Control (40)
 - - - x - - - 17 days argon (45)
 - △— 20 days air (48)
- (Tr in seconds)

25X1

25X1

25X1

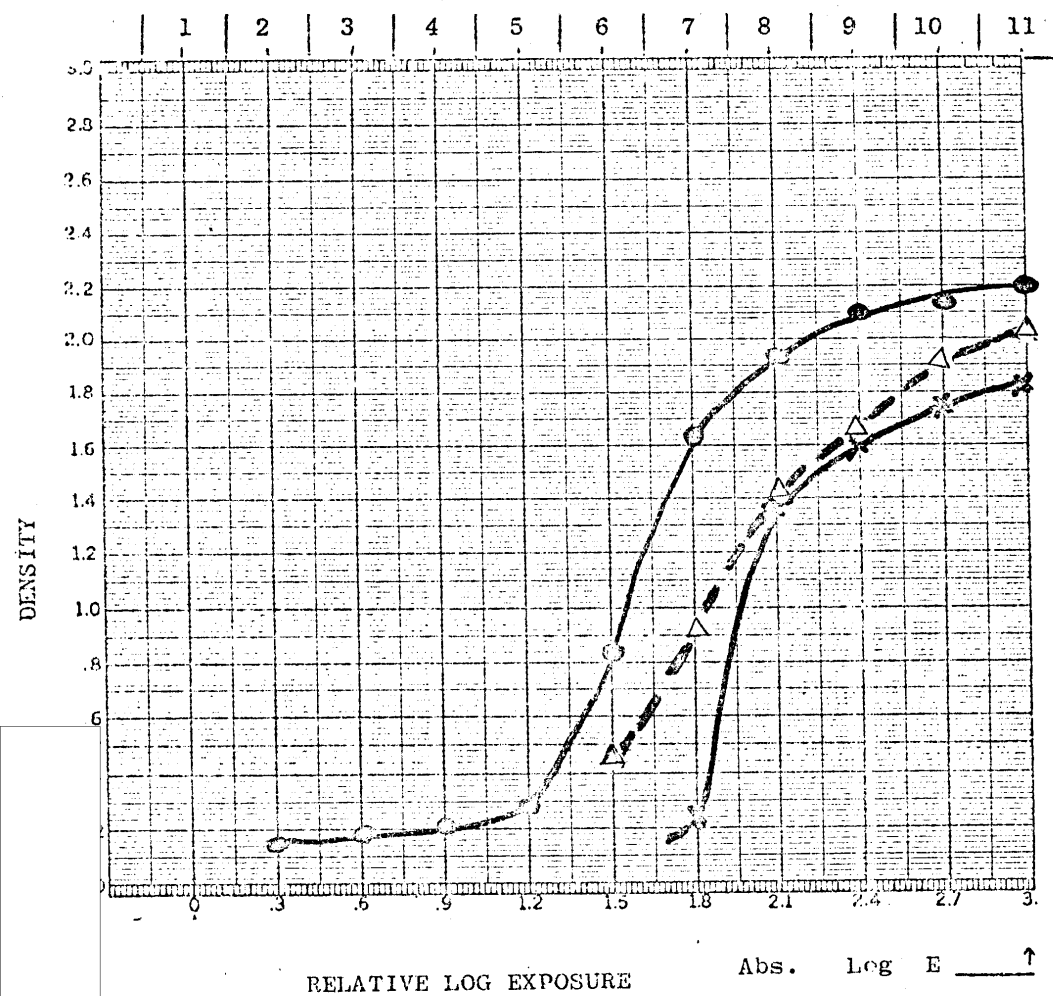


FIGURE 37
Ingredient Inter
Decay Study
5/D7 System
D260/4PO/D7/PS
RLD Mode

Legend

- 0 days Control (43)
- x— 17 days argon (49)
- - -△- - 20 days air (254)

(Tr in seconds)

25X1

25X1

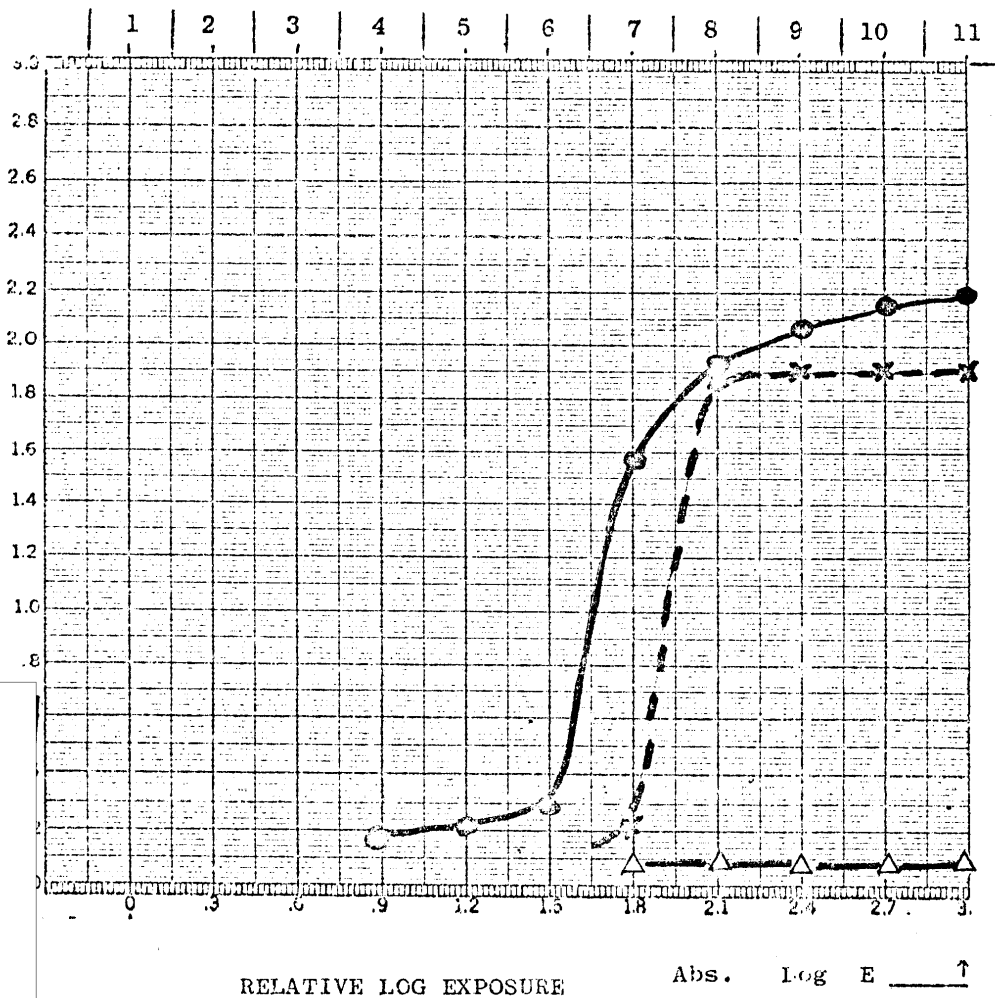


FIGURE 38
Ingredient Inter
Decay Study:
5/D7 System
D260/D7/PS
RLD Mode

Legend

- 0 days Control (46)
- - - x - - 17 days argon (45)
- △— 20 days air (300)

(Tr in seconds)

25X1

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1. Oxygen (air) plays a principal role in speed decay.
2. Oxygen's role is manifested as loss of density and increase in development time.
3. 4PO retards this decay.

However, the latest studies with 5/D8 indicate a significant contrast between D8 and D7, with D8 showing the more desirable properties. Thus, D8 shows better behaved D-Log E curves, less rapid decay and less tendency toward blotching. In fact, blotching is not nearly the problem it is with the 5/D7 system.

1.1.1.3.4 Coating Solution Decay

The measurement and study of speed decay has been complicated thus far by the inability to separate or totally differentiate the chemical decay from loss of activator. Overcoating with PVA prevents loss of activator, but the resulting behavior can not necessarily be attributed to chemical decay. Oxygen plays a role not only in speed decay but also in the normal photoinitiated reactions, and since the PVA overcoat excludes oxygen, the resulting photographic behavior cannot be attributed merely to chemical decay. Furthermore the PVA overcoat probably introduces a new set of parameters attributable to neither of the recognized causes of speed decay.

Only one means is presently available to observe and study chemical decay independent of the decay attributable to loss of activator. This involves studying the stability of bulk coating solutions from which the loss of activator can be prevented by keeping the solutions in stoppered bottles. The effects of oxygen can be included by comparing the stability of solutions, prepared and stored in the presence of air with solutions prepared and stored in the absence of air.

Formula 5/D8

The 5/D8 coating solution decays whether in air or oxygen-free, but there are significant differences. The D-Log E curves for the DPO mode are seen in Figures 39 and 40 and for the RLD mode in Figures 41 and 42. The complications of working in the

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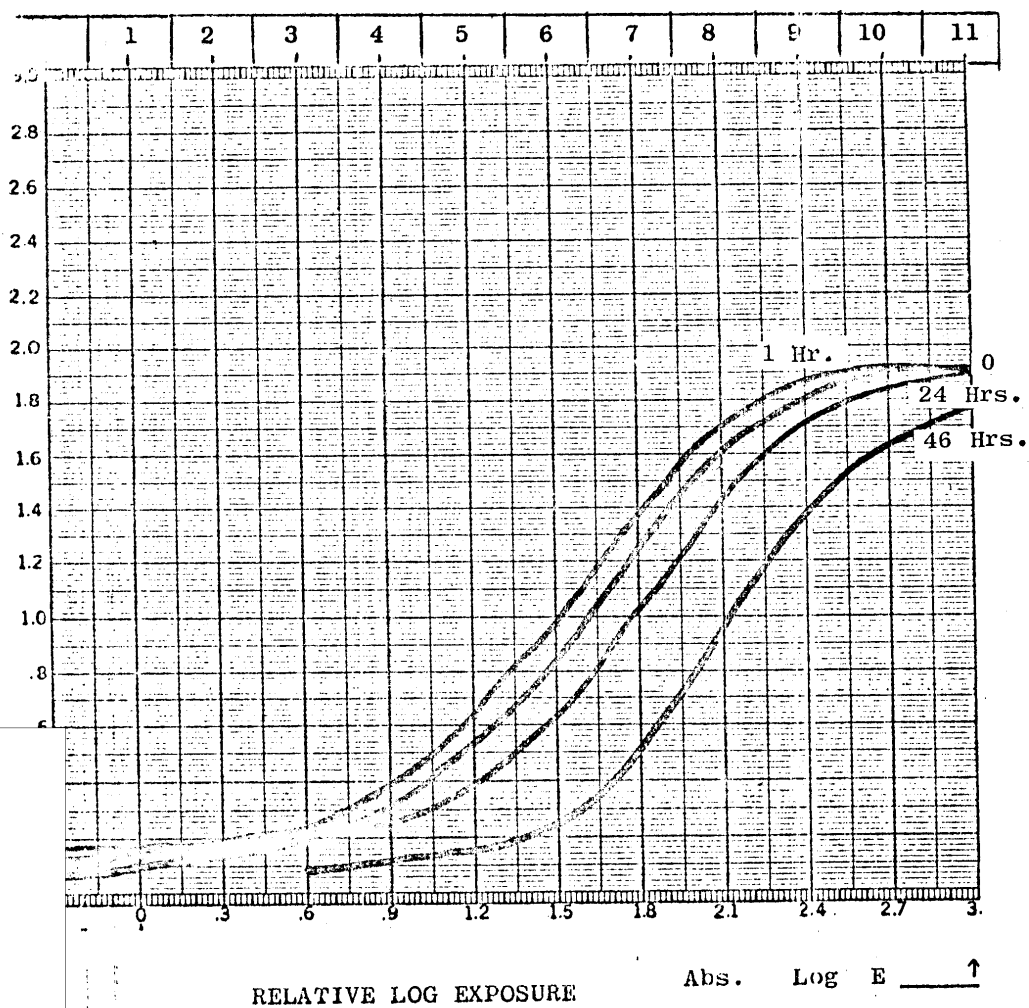


FIGURE 39
Coating Solution
Decay: In Air
Formula 5/D8
DPO Mode

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25X1

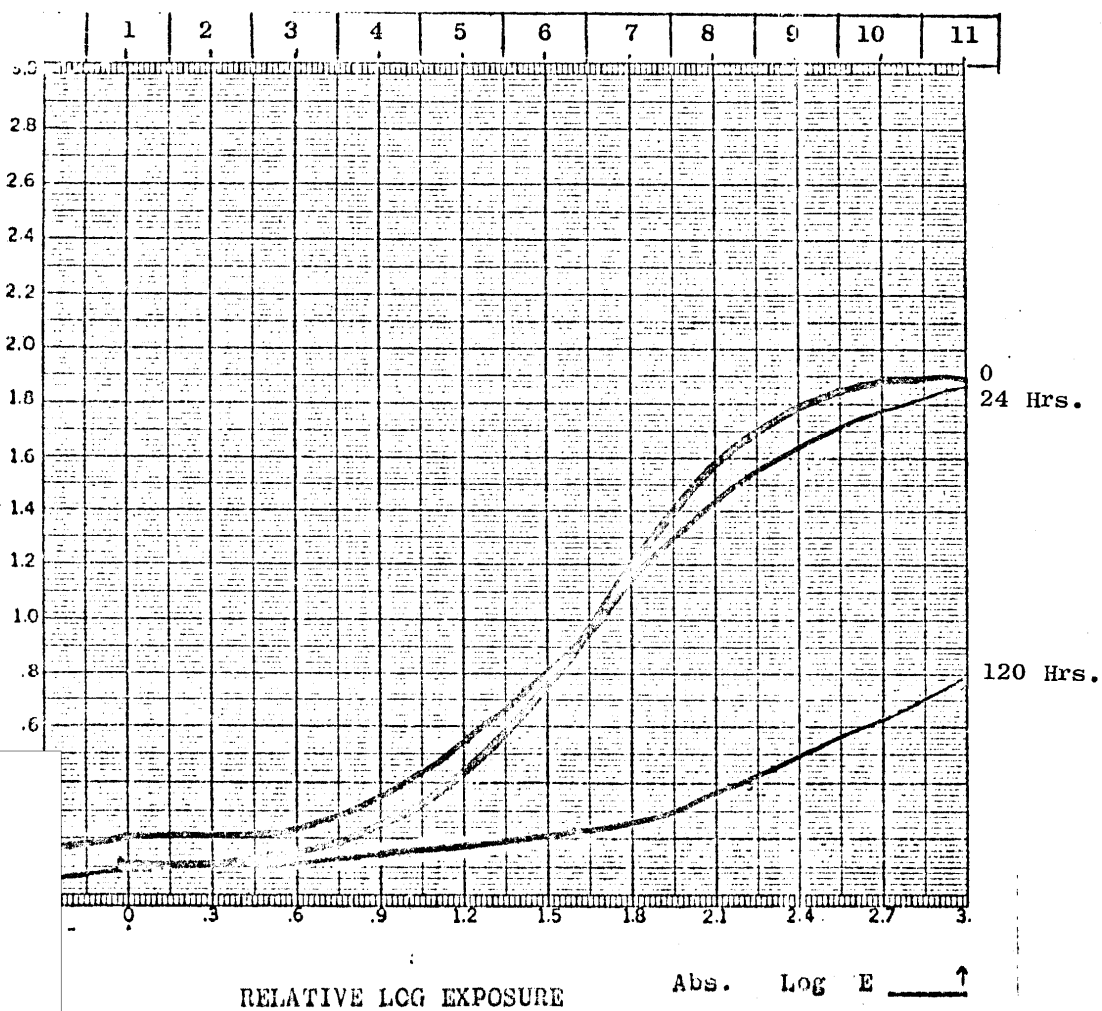


FIGURE 40
Coating Solution
Decay: Oxygen-Fre
Formula 5/D8
DPO Mode

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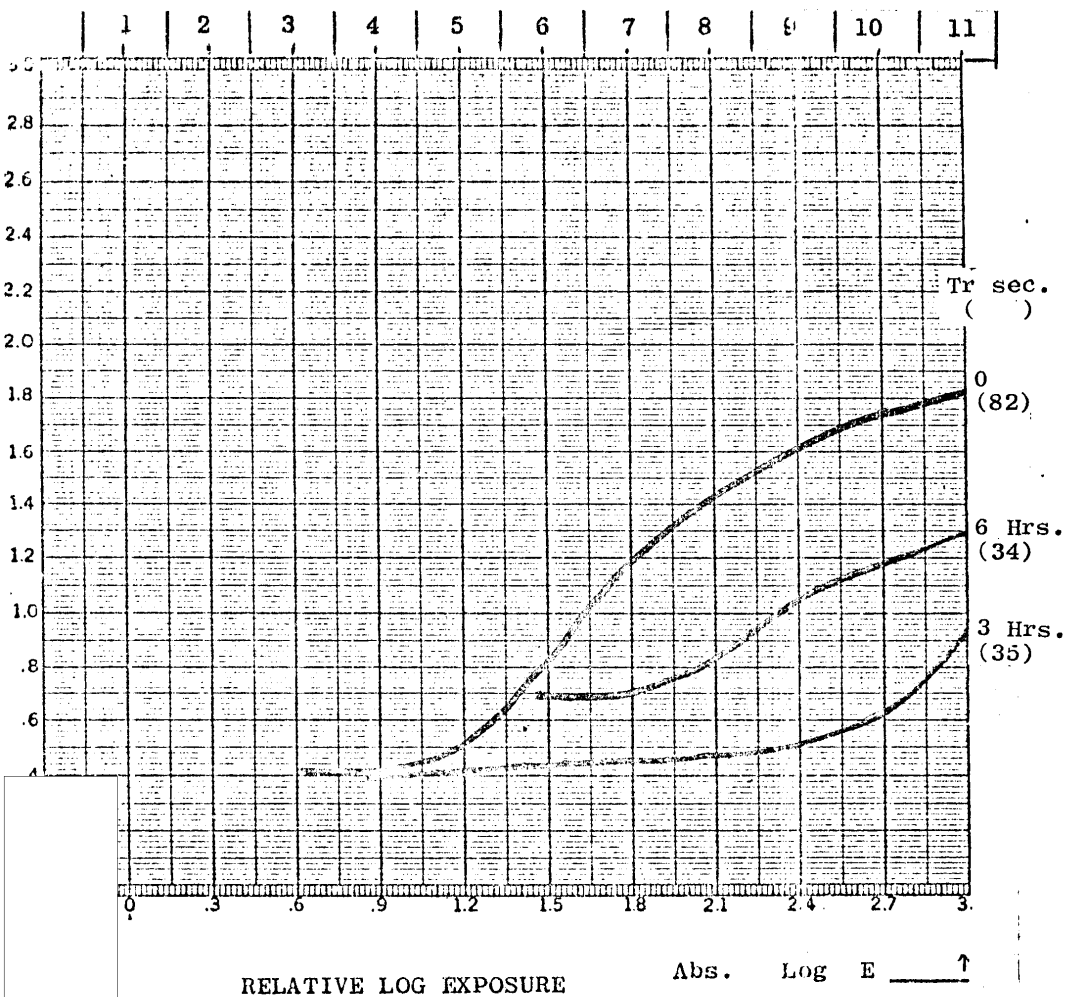


FIGURE 41
Coating Solution
Decay: In Air
Formula 5/D8
RLD Mode

25X1

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25X1

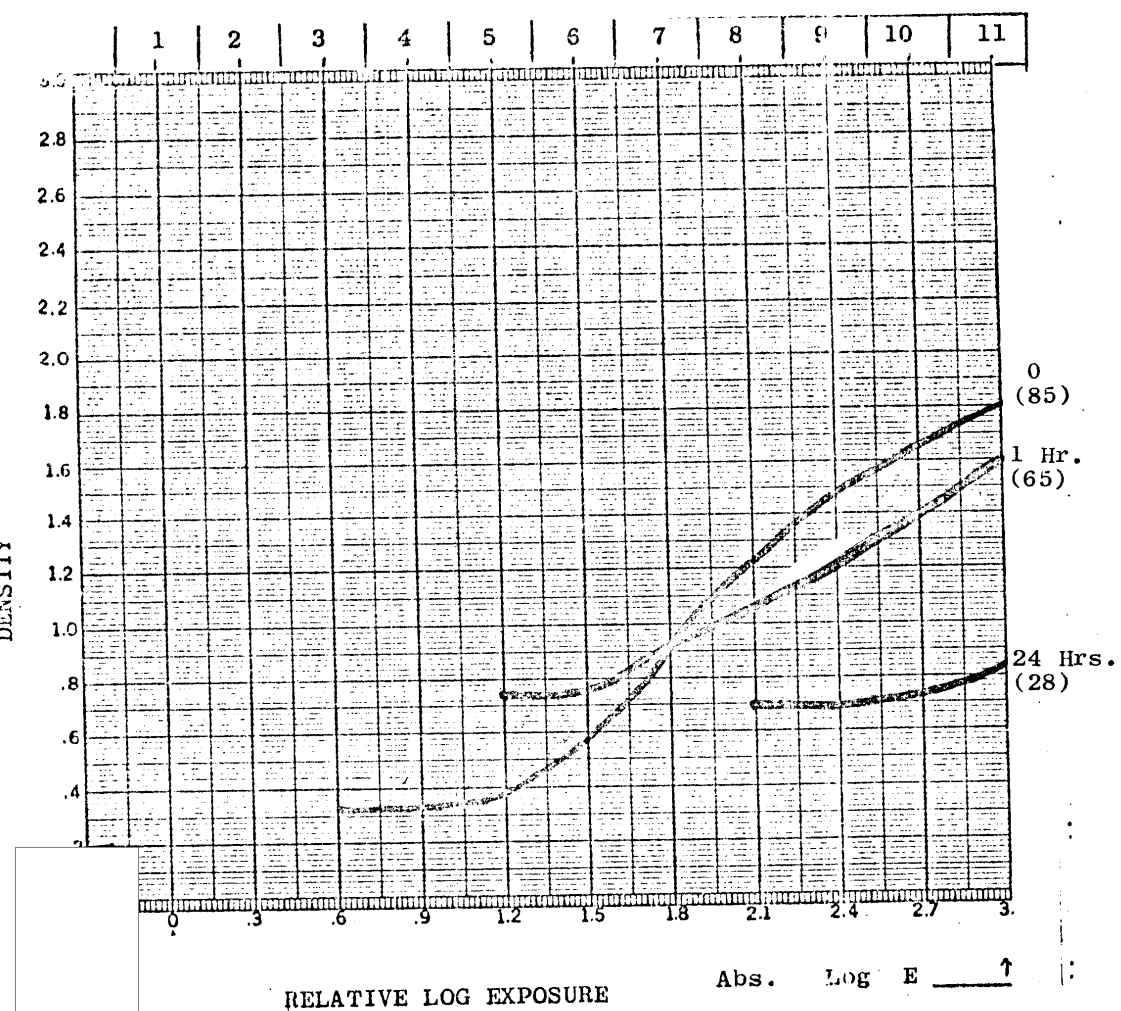


FIGURE 42
Coating Solution
Decay: Oxygen-Free
Formula 5/D8
RLD Mode

25X1

- 09 -

25X1

- 61 -

environmental chamber and the time involved make it difficult to obtain direct time comparisons for aging with and without oxygen. As a result, these figures are of little comparative value and essentially serve only to show that the solution changes.

Nevertheless, a change in image color accompanied the sensitometric decay. The image color of fresh 5/D8 is a deep purplish-blue but as the solution aged the image became sky-blue, the color of Formula 5 (D260) without D8 or D7. This visual change was evidenced by a change from the Wratten 93 (green) to the Wratten 102 (visual) filter for reading maximum densities. In the presence of air the color change occurred sometime between 6 and 24 hours, while in the absence of air the change occurred sometime between 1 and 5 days.

The RLD mode showed after 6 hours a very grainy background which is referred to as a sandpaper effect since unstable coating solutions which precipitate dye afford a film having that appearance and feel. This effect results from the precipitated dye particles. In this case, however, precipitated dye particles are not the cause of the sandpaper effect since the printouts did not show the effect. The effect may have been due to the same basic reason but in this instance the dye particles were submicroscopic and although they were invisible on direct printout, served as latent image centers which became visible on development.

Formula 5/D7

The 5/D7 coating solutions' behavior was similar to those of 5/D8 but with significant differences. The oxygen-free solution showed a color change from deep magenta to D260-blue sometime between 6 and 24 hours compared to sometime between 1 and 5 days for the 5/D8 solution. In the case of 5/D7, the color change was slower in air (just noticeable after 24 hours) than in the absence of air, which is just the opposite of 5/D8's behavior. During the period of this color change, dye precipitation was quite obvious as evidenced by a pronounced sandpaper effect in the DPO. However, after 72 hours the color change to D260-blue was complete and all precipitated dye had redissolved. Most interesting, however, was the following 72 hour period after which (144 hours) the sensitivity had increased. Comparison of the 72 and 144 hour solid curves in Figure 43 illustrates this phenomenon. The solid curves in Figure 43 were read with a Wratten 94 (blue) filter which is standard for this system. The broken curve corresponds to the same film, but was read with a Wratten 102 (visual) filter. The color change which has occurred is obvious.

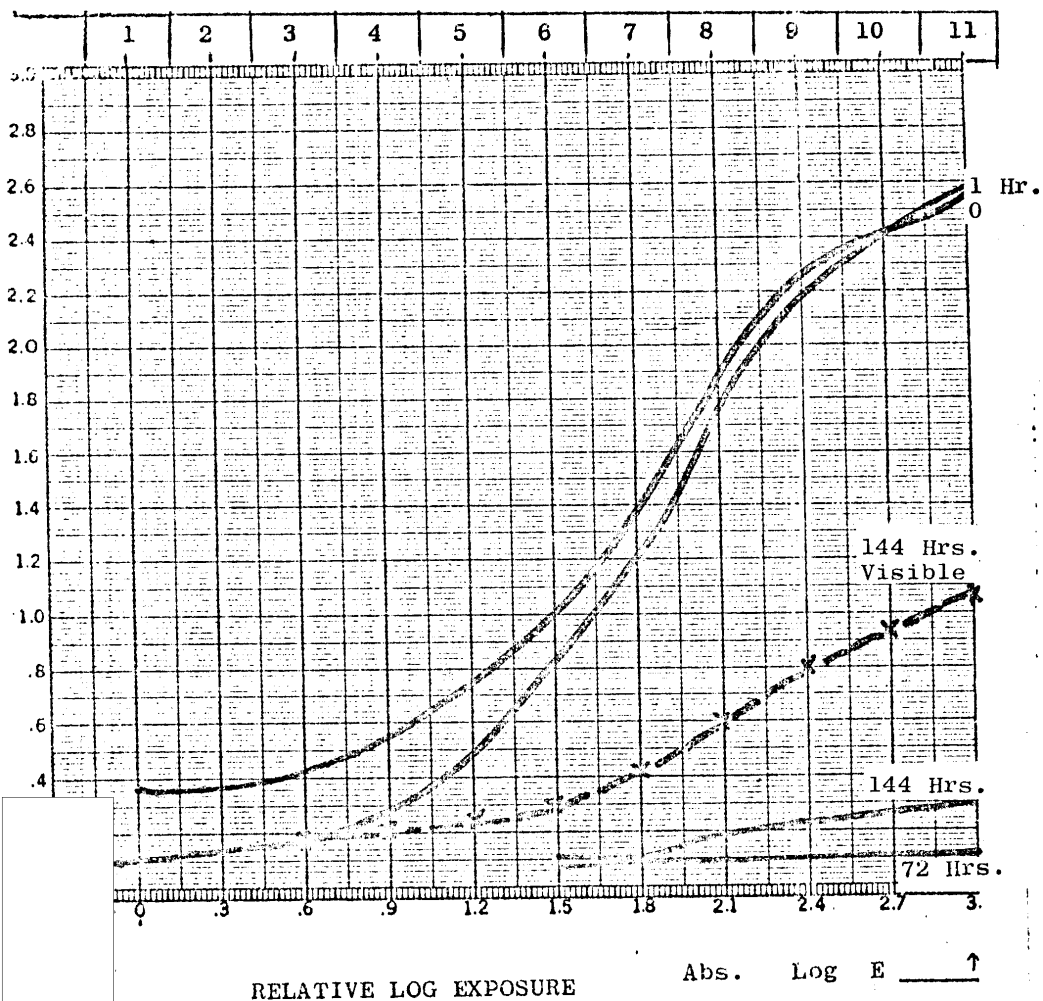


FIGURE 43
Coating Solution
Decay: Oxygen-Free
Formula 5/D7
DPO Mode

Solid Lines: Wratten 94
(blue) Filter
Dashed Line: Wratten 102
(visible) Filter

25X1

25X1

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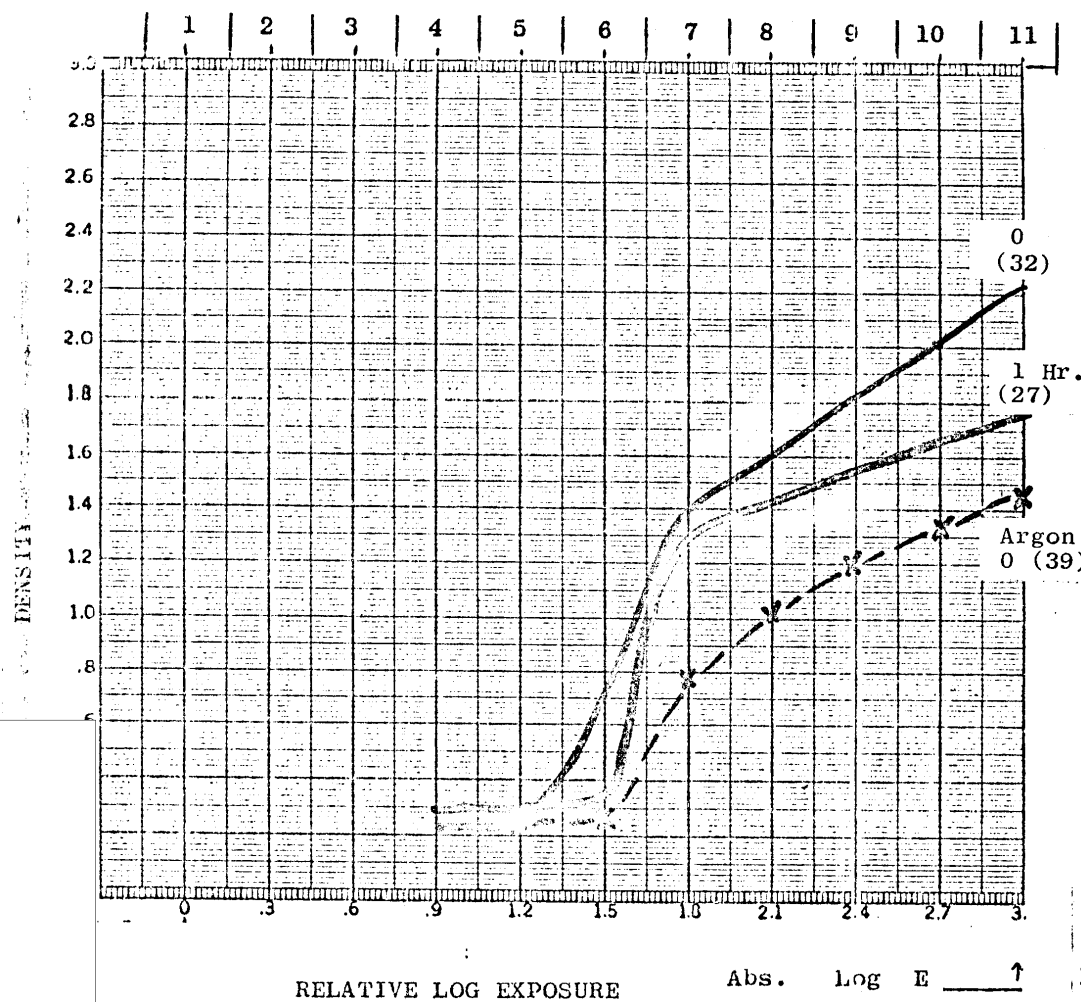


FIGURE 44
Coating Solution
Decay: In Air
Formula 5/D7
RLD Mode

25X1

- 63 -

25X1

- 64 -

The effect of oxygen was most noticeable in the RLD mode (Figure 44). The solid curves show the change after one hour in air. In the absence of air the fresh film is poorer and after one hour the film totally fogs with only 9 seconds of development time.

Though perhaps less convincing than previously presented data, here again it appears that Formula 5/D8 is superior than 5/D7 in that its coating solution is to some degree more stable.

1.1.2 Special Purifications

Special purifications of D260 involving recrystallization of photograde D260 from benzene/methanol under red light in the presence of antioxidants or peroxide decomposers were carried out, and the resulting D260 compared in films (Table 2).

The combinations of thiols and long-chain olefins (Table 2, Nos. 5 through 7) were tried on the basis that the two compound types react in the presence of peroxides to form sulfides of the type $\text{CH}_3(\text{CH}_2)_x\text{S}(\text{CH}_2)_n\text{S}(\text{CH}_2)_x\text{CH}_3$ (Table 1).

More extensive studies are anticipated and will include some of the more promising additives (Section 1.1.1.1) from the general screening and will include incorporation of the resulting D260 samples into the overcoating evaluations.

1.1.3 Synthesis Program

1.1.3.1 D260 and Analogue

1.1.3.1.1 D427 (D260-Anthrone)

The oxidation of D263 to D427 (Scheme 2) was accomplished using dimethylsulfoxide (DMSO) and air. Optimum conditions for synthesis and purification gave a 44% yield.

An attempt to isolate pure anthrone from crude samples containing anthranol by reaction with isocyanate failed: an alumina column impregnated with RC-805 isocyanate resin failed to trap the anthranol.

25X1

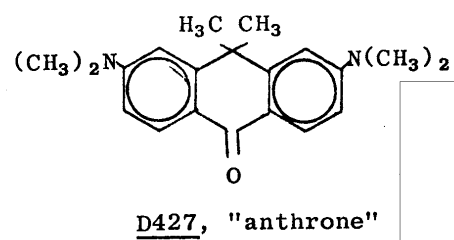
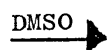
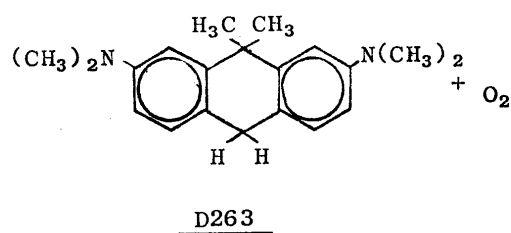
TABLE 2

Antioxidant Used	Comparison with Control	Reason
1. 1-octadene + 1-decene	much better	Higher Dmax, lower fog, high s both DPO and RLD
2. bis(tert-butyl)thiolsulfinate	slightly better	Dnet higher on 3 hour aging
3. 1-decene	slightly poorer	Slight blotch, DPO Dmax slightly lower
4. bis(tert-butyl) disulfide	worse	Dnet lower, high fog
5. 1,2-ethanedithiol + 1-decene	worse	Higher fog on DPO, blotch on RLD
6. 1,3-propanedithiol + 1-decene	worse	Lower Dmax, RLD blotch
7. 1,3-propanedithiol + 1-octadecene	worse	High fog, slightly lower Dmax, blotch starting
8. 1,2-ethanedithiol	worse	DPO increased fog, RLD complete blotch
1,3-propanedithiol	worse	DPO slightly higher fog, RLD complete blotch, low Dmax

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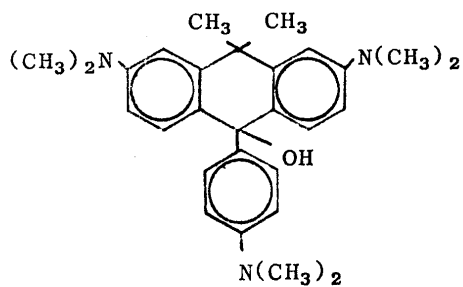
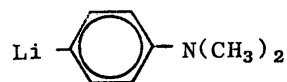
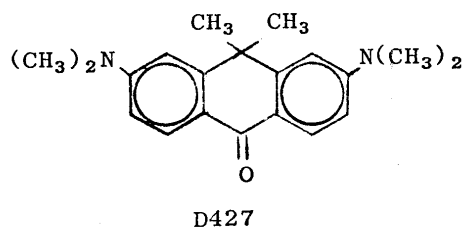
SCHEME 2



25X1

SCHEME 3

Synthetic Scheme for D431AN



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25X1

- 67 -

1.1.3.1.2 D431 (D260-Carbinol)

The planned synthesis of D431 involved addition of p-lithiodimethylaniline to the anthrone (D427) as seen in Scheme 3. Para-lithiodimethylaniline was first prepared from p-bromo-dimethylaniline and butyllithium using tetramethylethylenediamine (TMEDA) according to the procedure of Hallas and Waring⁷. Two attempts at this reaction were made using this procedure, and both failed. The TMEDA caused messy reaction mixtures from which D431 was inseparable.

A third attempt excluded TMEDA, according to the procedure of Aaron and Barker⁸. The reaction proceeded smoothly, affording 3 g of the chloride dye of D260 (D280AN, "AN" distinguishing products originating via the anthrone route) and 8.0 g of D260-carbinol (D431AN). The carbinol was a pale blue solid, mp 155-7°C, as compared to the reported mp 150-1°C: Calc'd for $C_{28}H_{35}N_3O$: C, 78.32; H, 8.15; N, 9.79; O, 3.73. Found: C, 77.92; H, 7.87; N, 9.07; O, 5.02.

The reaction was accompanied by formation of tetramethylbenzidine (TMB). It should be remembered that TMB was a detrimental impurity in D260 prepared by the conventional route. It is present in Michler's Hydrol, an intermediate in that route, but is no longer a problem since the Michler's hydrol is pre-purified. Fortunately, TMB is easily removed from both the carbinol and the dye (which contrasts with its exceedingly difficult separation from D260) and it therefore poses no problem.

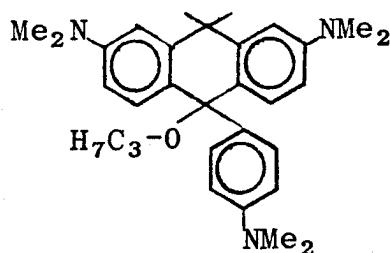
The anthrone route to D260 was originally believed to be a means of avoiding TMB, since Michler's hydrol was not used and no other potential source could be envisioned. It should have been obvious, however, that p-lithiodimethylaniline could oxidatively couple to give TMB, a reaction which is analogous to the well known oxidative coupling of Grignard reagents.

1.1.3.1.3 D260AN

D260-carbinol (D431AN), prepared as described in the preceding section, was reduced with zinc in acetic acid. Workup of the reduction mixture gave a solid which evaluated as D260 in Formula 5/D7 gave a green precipitate and no image by RLD. DPO gave a red image indicating no D260 activity. Workup also gave a benzene solution which upon freeze-drying afforded a solid material which was also evaluated as D260 in 5/D8. It also gave no image by RLD and a gray-black image by DPO. Elemental analysis agrees with the propyl ether of D260 (I).

25X1

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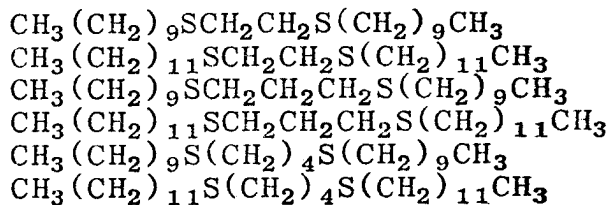
I

Thus far authentic D260 has not been isolated from the anthrone route, but this appears near term, since D260-dye obtained by oxidation of D260 has been successfully reduced by zinc in acetic acid. Additional work is justified in order to compare photographic activity and speed decay properties with those of D260 prepared by the customary route. This work has been temporarily suspended, however, due to other immediate priorities.

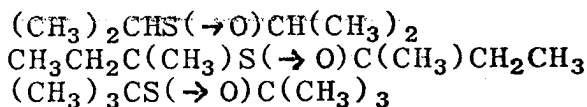
1.1.3.2 Peroxide Decomposers

The following antioxidants and peroxide decomposers were synthesized and purified since July 1.

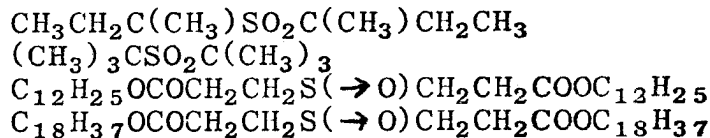
Sulfides:



Sulfoxides:

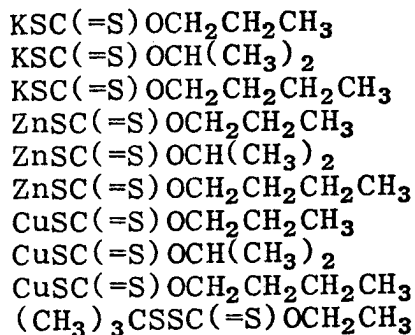
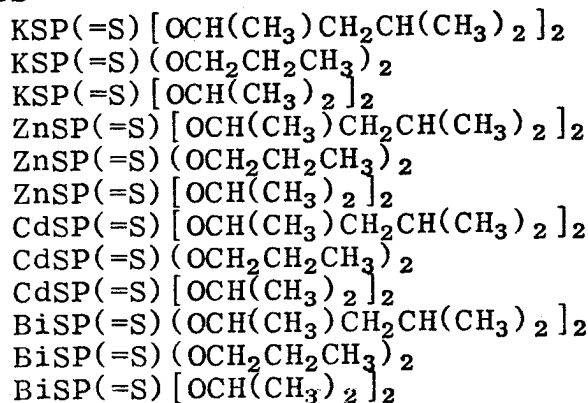
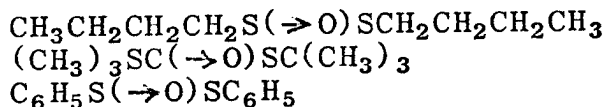
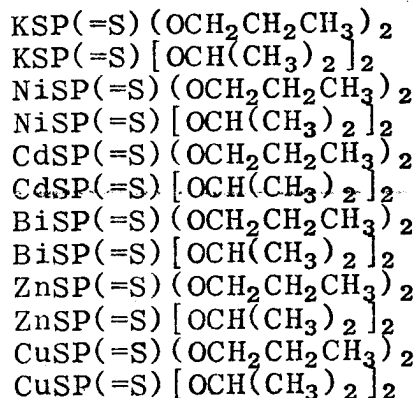


Sulfones:



25X1

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Xanthates:**Dialkyl Dithiophosphinates:****Thiosulfinates:****Thiolthionophosphonates:**

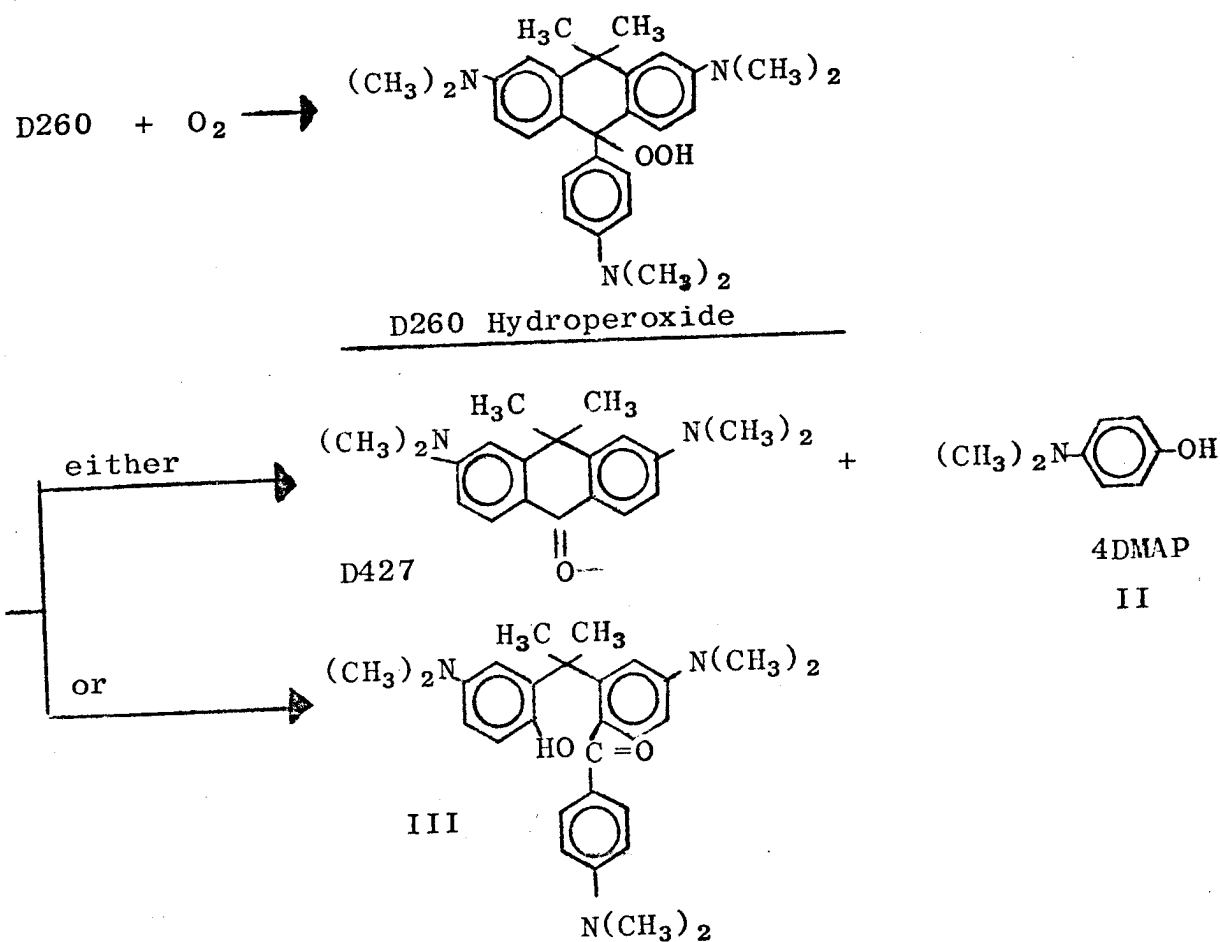
25X1

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1.1.3.3 Synthesis of D263

D263 is a leuco anthrancene which has shown great promise in preliminary experiments as a potential replacement for D260. It has comparable or better photosensitivity and there is reason to believe that the structure would be less susceptible to speed decay caused by autoxidation.

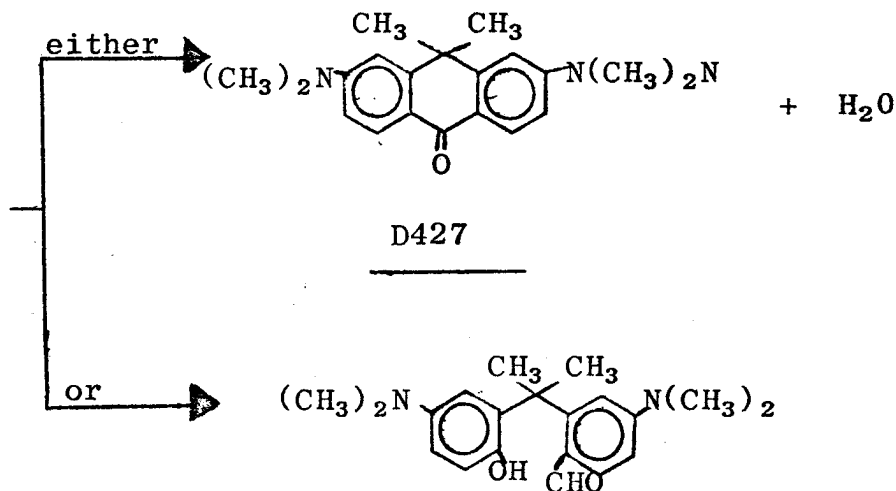
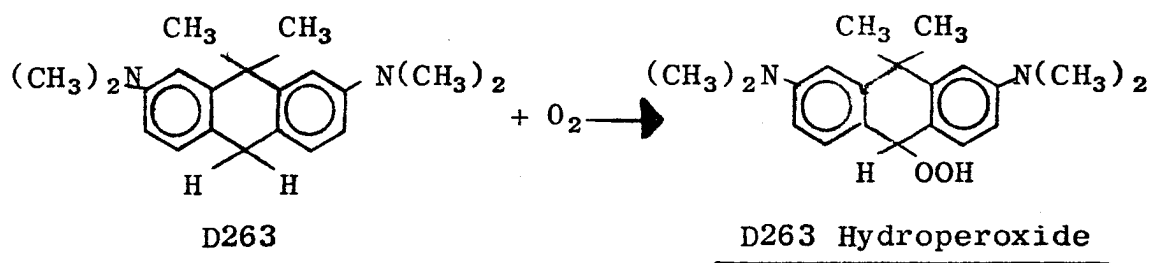
D260 is oxidized to its hydroperoxide which can decompose to form two different phenolic products, 4-dimethylaminophenol (4DMAP, II) and a complicated benzophenonephenol (III). Either phenol causes speed decay by terminating the free radical reaction.



25X1

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The corresponding decomposition of the hydroperoxide of D263 should lead to fewer deleterious phenolic products.



2-[2-(2-formyl-5-dimethylamino)-propylidene]-5-dimethylaminophenol

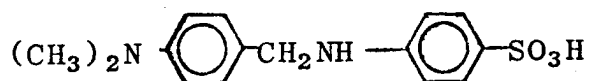
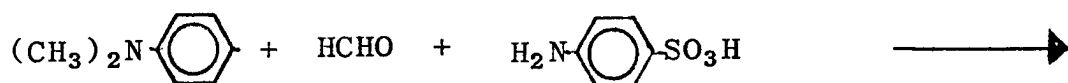
It can be seen that either of the two most probable decomposition routes of the D260 hydroperoxide leads to a phenol while only one of the two routes of decomposition of D263 hydroperoxide leads to a phenol. Any or all of these phenols would be expected to cause chemical speed decay.

D427 (the "anthrone"), formed in both schemes, has no effect on speed decay. The fewer phenolic products formed in the D263 scheme supports our hope that this leuco will be significantly improved in the respect to speed decay.

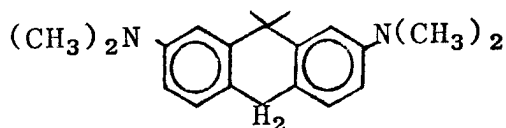
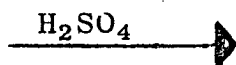
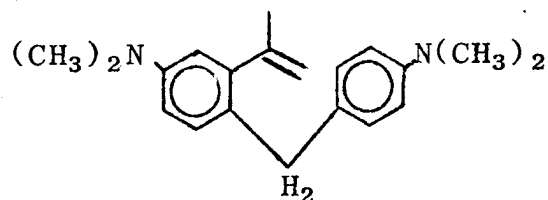
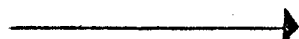
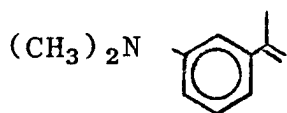
- 72 -

In comparison with D260, the synthesis of D263 is much simpler, the purification is easier, and the leuco is more photosensitive (darkens during laboratory manipulations).

D263 can be prepared from dimethylaniline, formaldehyde, sulfanilic acid, and 2-(m-dimethylaminophenyl)propene by the following sequence of reactions⁹.



N-p-dimethylaminobenzylsulfanilic acid



D263

Two syntheses of D263 were carried out during this period. The literature preparation was improved by reducing the solvent volume in the first and second steps by a factor of three each, and by reducing the sulfuric acid volume in the final condensation step by a factor 7.5.

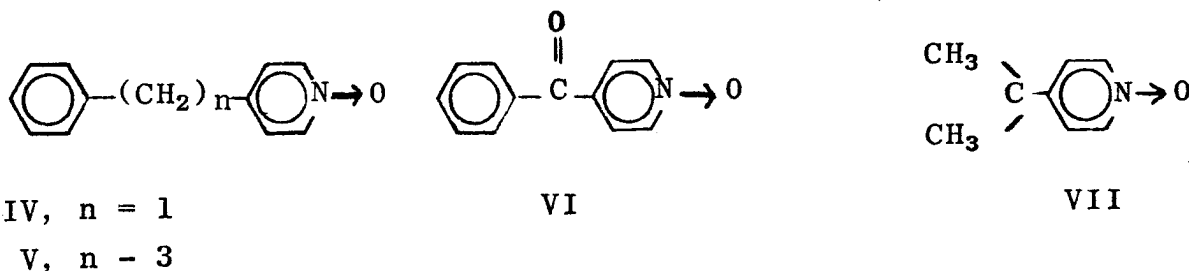
- 73 -

The leuco was isolated by elution from a column of basic alumina. After recrystallization very large white crystals were obtained.

Preliminary film evaluation is currently underway. Of immediate interest is the relative rate of spot growth compared to 5/D8 and 5/D7 and relative rate of speed decay of unover-coated film.

1.1.3.4 Synthesis of New N-Oxides

4-Benzylpyridine-N-oxide (IV), 4-(3-phenylpropyl)pyridine-N-oxide (V), 4-benzoylpyridine-N-oxide (VI), and 4-isopropylpyridine-N-oxide (VII) have been prepared.



Analyses for IV, V and VI were good. VII has been sent out for analysis.

IV and V have been found to be more soluble in benzene than 4PO, which should be an improvement in film formulation.

Under preparation at this time are 2-, 3- and 4-pentadecylpyridine-N-oxide; 2-, 3- and 4-(n-hexyl)pyridine-N-oxide; 2-, 3- and 4-tridecylpyridine-N-oxide; and 2- and 4-(n-octyl)pyridine-N-oxide. It is expected that these, too, will show improved benzene-solubility.

1.1.4 Ingredient Purification and Supply Maintenance

1.1.4.1 D260

A superior sample of D260, in comparison with earlier "good" samples, is designated Sample CS4G4. D260 in benzene

25X1

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was put onto a basic alumina column, eluted in red light with 95/5 benzene/ethyl acetate, solvent removed under vacuum, solid ball milled with glass marbles, and recrystallized from benzene and methanol under red light. The crystals were dried under vacuum, ground with a mortar and pestle and redried under vacuum.

Three other samples of D260 were purified to yield material of photograde quality, but not as good as Sample CS4G4.

A shipment of 600+ grams of D260 received from ChemSampCo in September did not clean up as easily as earlier shipments. Photograde material was obtained but at significantly lower yield than usual.

1.1.4.2 Image Enhancers

A 350 gram sample of D7 was prepared by base-catalyzed condensation and recrystallized. This is a departure from earlier acid-catalyzed procedures. The basic procedure was expected to be superior because it eliminates the possible conversion of any of the styryl base to the much more highly colored styryl dye, and initial results support this expectation.

A similarly base-catalyzed preparation of D8 was carried out on a large scale, resulting in an improvement in yield and quality. This will become the new standard D8 synthesis.

1.1.4.3 Purifications

All future purifications will avoid the use of sintered glass funnels and ceramic mortars and pestles (see Section 1.1.1.2.3).

1.1.5 Analytical Studies

1.1.5.1 Dust Samples

Six dust samples collected from darkrooms were analyzed qualitatively for film ingredients. The results show occasional presence of such materials as D7 and D392 (the dye of D260).

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1.1.5.2 4DMAP Assay of Aged Solutions

4DMAP was assayed in aged D260 solutions by TLC. A solution containing only D260 and polystyrene showed the presence of considerable 4DMAP. In contrast to that result, aged solutions of D260 with D7, 4PO, or both showed no detectable phenol.

An aged solution of D7 and 4DMAP showed that 4DMAP was not consumed under those conditions.

A fresh Formula 5 film was prepared. Sections were extracted with benzene at intervals. No 4DMAP could be detected after 24 hours (Section 1.1.1.3.2.2).

1.1.5.3 Polyvinyl Alcohol

The polyvinyl alcohol (PVA) used for overcoating was passed through acidic and basic ion exchange columns to remove foreign materials. After this treatment the pH was 5.6.

An alternate to the time-consuming passage through the columns, later samples were merely slurried as a 15% solution (in the case of DuPont Elvanol 51-05) with Rexyn 101, a sodium cation exchange resin. Trace metal analyses were determined spectrographically on slurried and on untreated PVA. Levels of lead, mercury, selenium, and barium were below the level of detectability. Levels of antimony, cadmium, and arsenic were apparently lowered by the slurry treatment from less than 10 to less than 1 ppm.

1.1.5.4 Film Dye Identification

Products from Formula 5/D7 coatings were extracted, fixed and separated from polystyrene to yield 20.6 grams of red-brown dye. A total of 488 fractions were collected from elution from basic alumina and were combined to make seven consolidated fractions. The product mixture is evidently quite complex. The only products identified were CBr_4 and 4-picoline. Presence of CBr_4 probably indicates incomplete fixing, as it had been found earlier that fixing of thick coatings of this type required repeated solvent extraction to stop photochemical activity. 4-Picoline was found corresponding to 10% of the 4PO originally present, indicating oxygen-donation as at least a partial role for 4PO. However, it must be established that the 4-picoline results from reactions in the film and not as an artifact of the chromatography.

25X1

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Irradiation in the "Merry-Go-Round" photochemical reactor of the ingredients of Formula 5/D7 was consistent with the above extraction results and contributed no new information. Similar irradiation of the ingredients of Formula 5/DPA resulted in no DPA or 4-picoline detectable by gas chromatography.

The separation of dye products has proved to be difficult and will necessitate using more appropriate and sophisticated separation techniques than thin layer chromatography (TLC). The feasibility of using such techniques as partition chromatography and electrophoresis is being explored as time permits, but any further attempts to separate and identify products is being discontinued for the remainder of this contract.

25X1

		DOC						EOC
		Jul	Aug	Sep	Oct	Nov	Dec	
1.1	Chemical R & D							
1.1.1	Inhibition of Speed Decay							▽
1.1.1.1	General Screening of Chemical Inhibitors							▽
1.1.1.2	Combined Chemical/Overcoating Methods							▽
1.1.2	Special Purifications				▽			
1.1.3	Synthesis Program				▽			
1.1.3.1	D260 and Analogue		▽					
1.1.3.2	Peroxide Decomposers				▽			
1.1.4	Ingredient Purification and Supply Maintenance							▽
1.1.5	Analytical Studies							▽

25X1

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25X1

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1.2 ENGINEERING

The engineering tasks for the first half of this contract have proceeded on schedule. Good progress has been made in most areas and significant improvements in both the results and techniques used have been shown.

Work on 1.2.4, Red Lite Testing, suspended during August/September because of the increase manpower necessary for completion of 1.2.2, was resumed as of 1 October, 1972, and is progressing well.

1.2.1 Calibration and Maintenance

Calibration and maintenance of all equipment have proceeded on schedule. Techniques for calibration have been improved for red lite development and sensitometer units. A more unified positioning system for probes and an on-site measuring technique have been developed. Improvements in the operation of the sensitometers and coating plates have reduced operator errors and operation time, and have improved accuracy.

1.2.2 New Darkroom Facilities

A new environmentally controlled darkroom facility was designed based on data previously obtained from controlled laboratories in project areas. The design of the facilities was begun July 1, and an area containing three laboratory coating rooms, a weighing room and a data reduction room has been completed. Construction was begun the first week in August and completed in the second week of September. This included a free-standing, self-contained laboratory with environmentally controlled air conditioning, dehumidification, water wash and particulate filter air handling system. Particular care was taken to reduce contaminants, to control temperature and humidity and to give optimum comfort to the technicians. The unit is designed with a dressing area, so that special clothing can be worn to reduce the introduction of contaminants from street cloths and from normal body tissue. One lab has a large exterior door for the introduction of large test equipment. Each laboratory has two compartmentalized coating hoods and a red lite and sensitometer hood. The area will hold a maximum of six technicians, all working independently. Coating operation began in these environmental laboratories on 2 September 1972.

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All the necessary equipment for weighing, mixing, coating, developing, fixing and recording of data has been constructed and/or obtained by engineering and is in place in the new dark-room area. This includes the normal compliment of services such as safe lights, vacuum stations, heaters, mixers, coating bars, cutting stations, static elimination bars, etc. In addition, six coating stations, three sensitometers, and three HID-2 red lite development units were constructed and placed in the unit. Items such as special filters dichroics, and an inventory of Marc 300 lamps for the red lite units has been stocked for use during the remainder of the program.

1.2.3 Shelf Life

Work has proceeded in this area with the main thrust aimed at eliminating the spots which occur in the overcoated mode.

1.2.3.1 Overcoating

Considerable progress has been achieved and samples of 5/D7 have been held for periods as long as 72 hours at room temperatures. Figures 45 and 46 show the sensitometric curves of four samples cut from the same sheet and then stored at 70°F. Figure 45, Curve 1, is the initial sensitometric curve and Curve 2 is the curve at 24 hours. Sensitivity in the printout mode has decreased at this point only a factor of 2. There has been a considerable speed loss in the printout mode at 72 hours, Curve 4, but the film does exhibit some sensitivity to a 10 second exposure and is completely clear of spots in the image area.

1.2.3.1.1 Equipment

A spin coater has been designed and built in-house to satisfy the specific needs of our coating operation. The unit operates from zero to 500 rpm and is capable of achieving a considerable range in coating thicknesses. The coating uniformity has not improved sufficiently at this point to allow spin coating of the sensitive layer, but is quite adequate for the overcoating work in progress. The size of the spin coater, however, limits its location and it cannot be placed inside the clean air hood. This allows dust particles, etc., to land on the sensitive coating during the transition period between coating in the hood

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and moving the sample to the spin coater. Improvements are being made to alleviate this problem. Samples overcoated on the spin coater consistently show no printout speed loss for periods up to 6 hours on the Formula 5/D7 film system. Experience on the spin coater has shown an improvement in both speed decay curve and a reduction in the number of spots as the percent coating solution or the number of overcoats is increased. At this point the optimum spin overcoat solution appears to be PVA 52-22, 8% by weight in water and a quadruple overcoat.

1.2.4 Red Lite Development

A novel system for optically developing 325B film samples has been devised. In the past no quantitative system of viewing the development process was possible. Such a system has now been shown feasible and indeed substantial amounts of data have been accumulated.

The system consists of a Beckman DK-2 scanning spectrophotometer with a time drive adaption which makes it possible to set the development radiation at a particular wavelength and allow the chart recorder to record changes in transmission occurring during the development process. This technique when fully exploited will provide a most powerful tool for obtaining pragmatic parameters and data for a thorough understanding of red lite development as employed with the 325B film materials!


The schematic diagram of the development apparatus is shown in Figure 47.

The film sample, which is placed across both the sample and reference beam is exposed on the sample side and left unexposed on the reference side. An accurate monitoring of any fog buildup is thereby accomplished since the slit will start to open should the reference beam intensity decrease.

Two curves have been included showing the rate of transmission change per unit time to the development radiation (Figure 48). No. 1 is an overcoated sample red lite developed at 650 nm and No. 2 is another overcoated sample red lite developed at 665 nm. The data associated with each curve is detailed below:

	No. 1	No. 2
Film Type:	Formula 10	Formula 10
Development λ :	650 nm	665 nm
Development Time:	3 Minutes	7 Minutes

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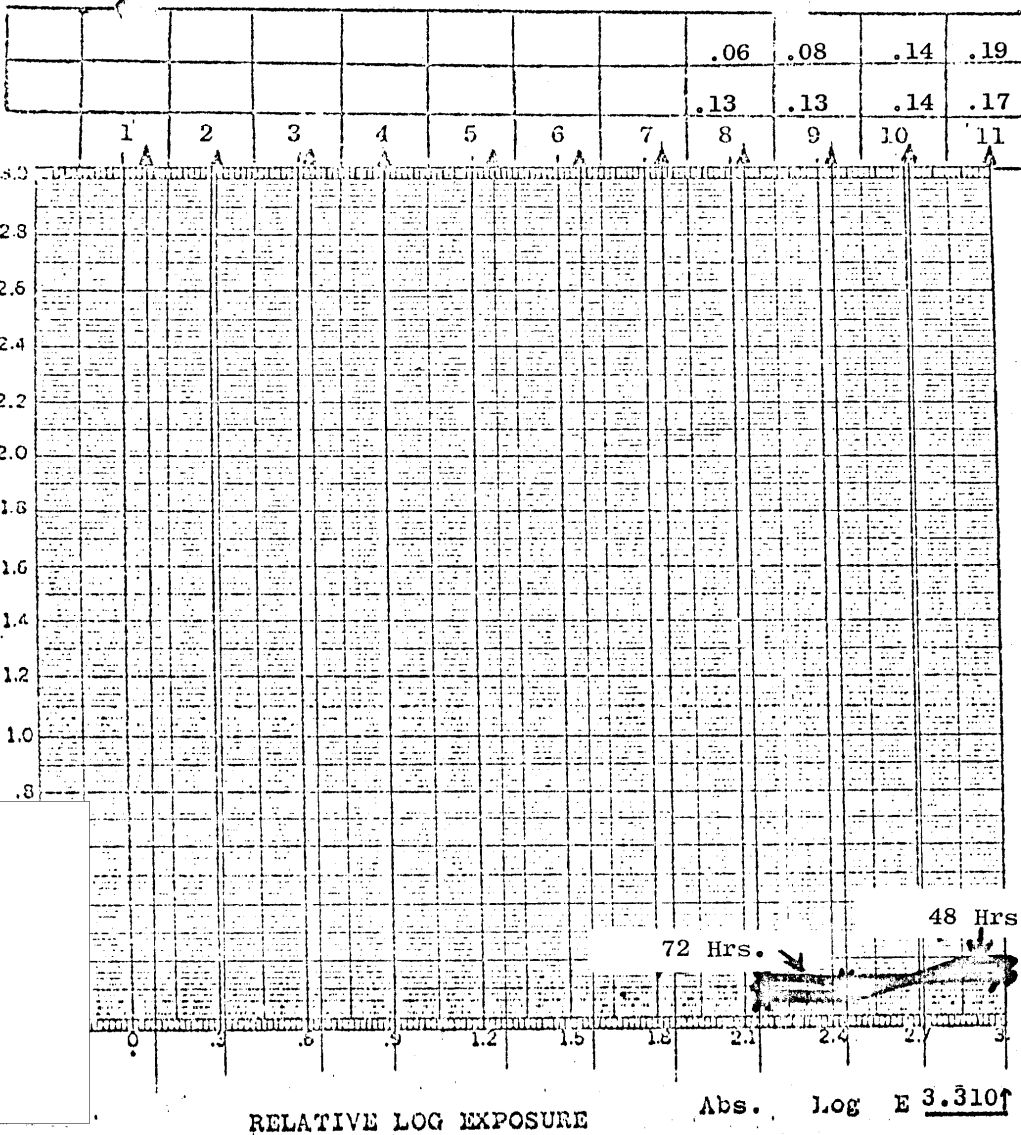


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	No. 1	No. 2
Dmax:	.55	1.35
Dmin:	.39	.05
Overcoat:	Dip PVA-52-22	Dip PVA-52-22
Bandwidth:	<u>+5</u> nm	<u>+5</u> nm

There are several obvious differences between the two samples. The rate of density amplification is much greater for the 650 nm sample but is prevented from complete amplification due to rapid fog buildup. The contrary is true for the sample developed 665 nm. Although the amplification rate is slower, a much higher Dmax is attained with the lower fog.

Unfortunately, complete step wedges can not be developed due to the small format size. This new procedure has opened new avenues to the control and understanding of the red lite mechanism.



FORMULA 46
DPO LIFE STUDY
Formula 5/D7

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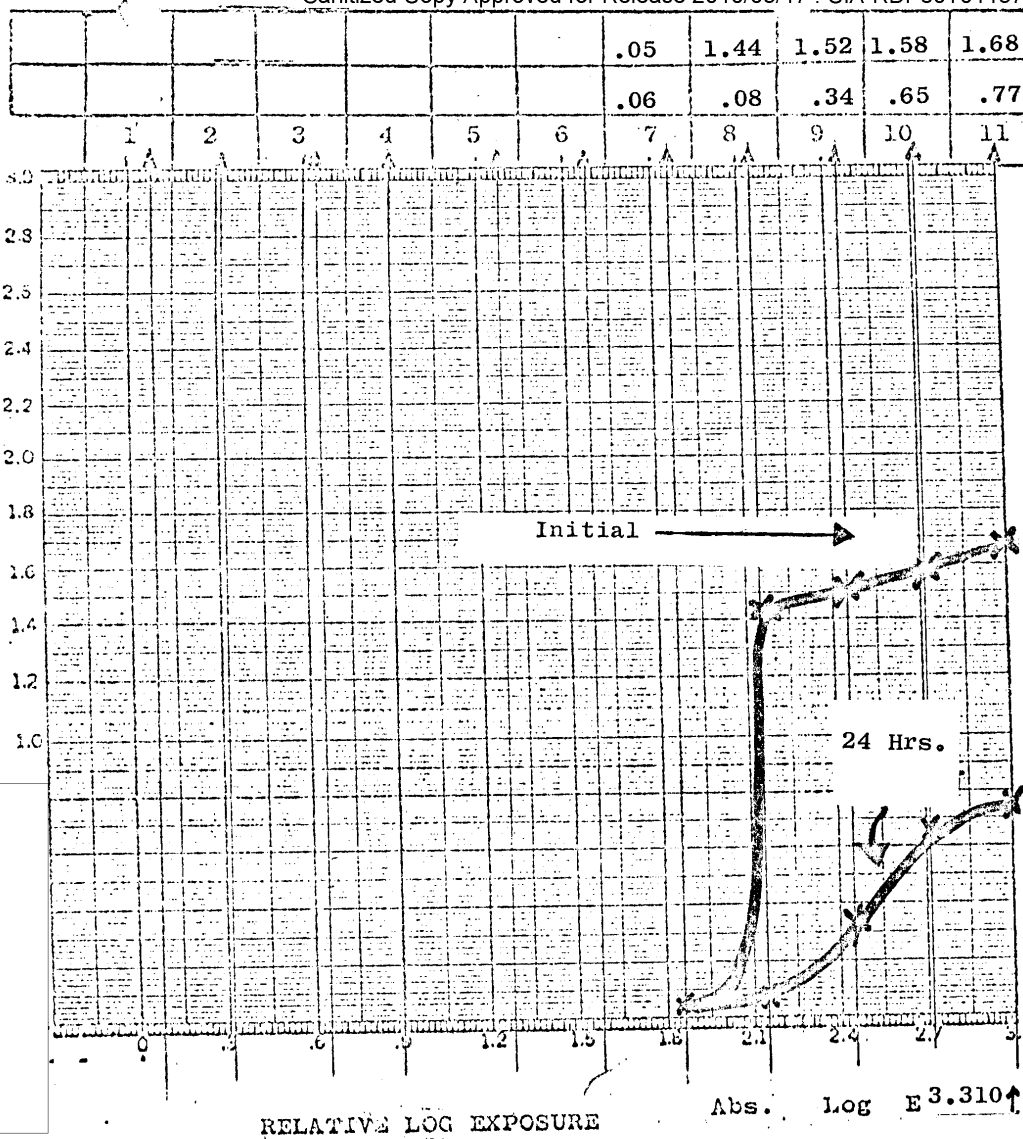


FIGURE 45
DPO LIFE STUDY
Formula 5/D7

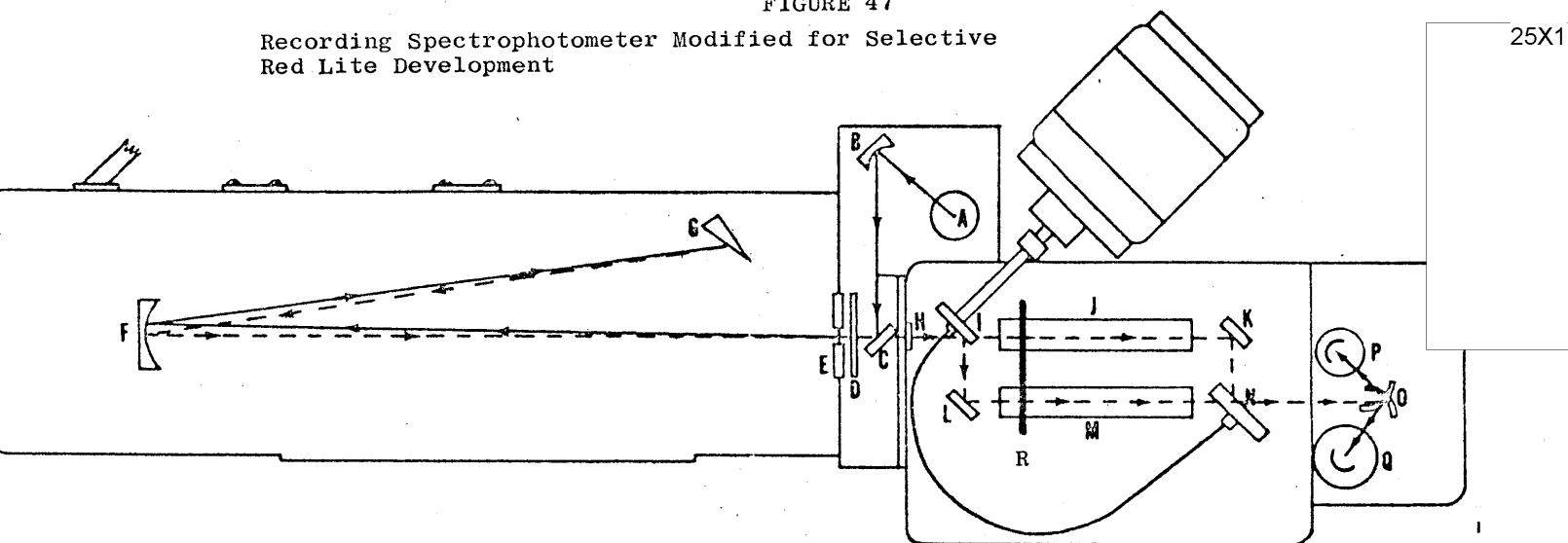
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FIGURE 47

Recording Spectrophotometer Modified for Selective
Red Lite Development



A - Light Source
B - Condensing Mirror
C - Entrance Mirror
D - Chopper
E - Slit
F - Collimating Mirror
G - Quartz Prism
H - Lens
I - Rotating Mirror

J - Reference Beam Path
K - Mirror
L - Mirror
M - Sample Beam Path
N - Rotating Mirror
O - Spherical Condensing Mirror
P - Lead Sulfide Detector
Q - Photo Multiplier
R - Film Sample:

Exposed side in sample path M.
Unexposed side in Reference path J.

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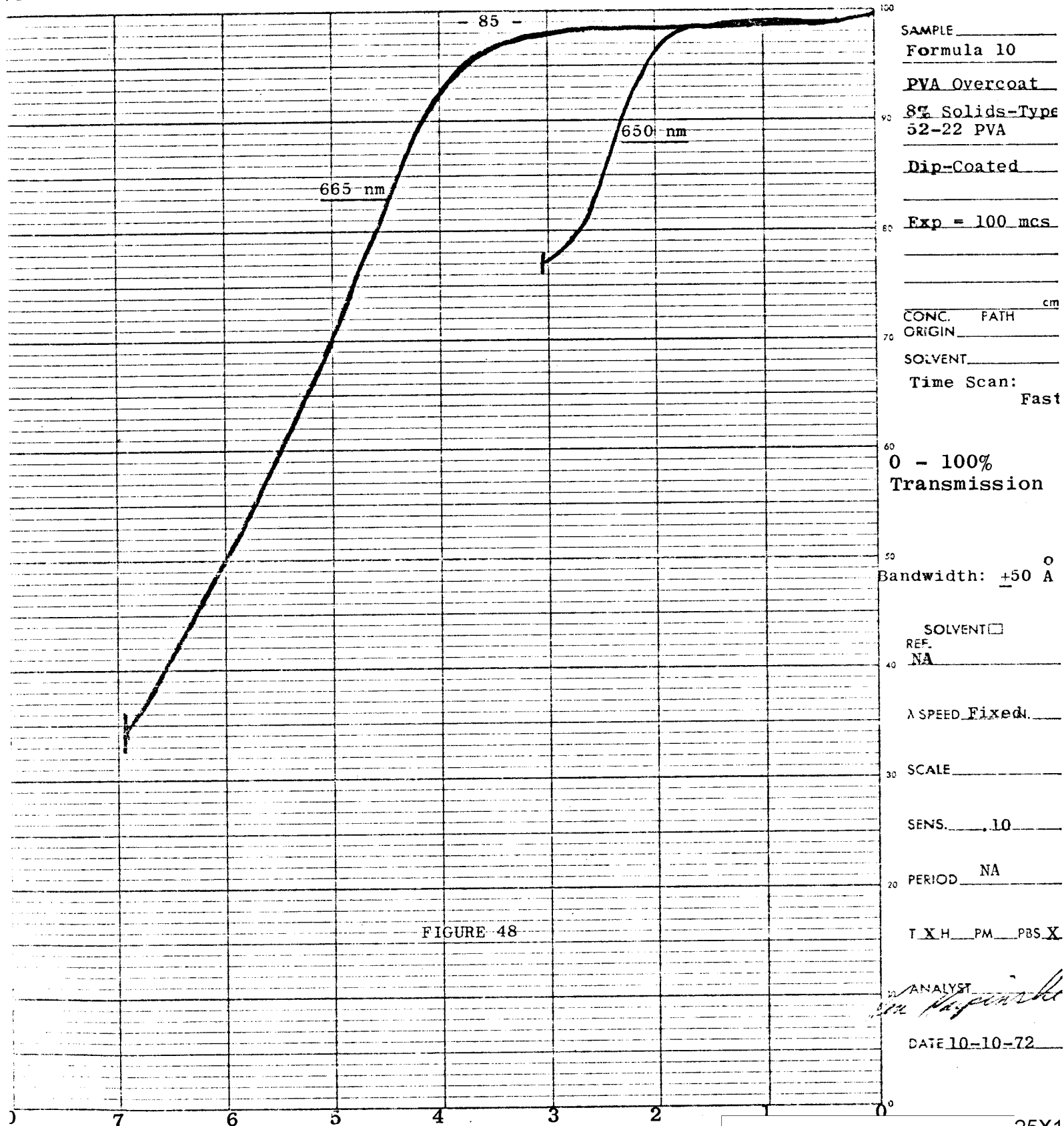
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WHEN REORDERING SPECIFY CHART NO. 12980

BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.

DK-2 CHART



		DOC	Jul	Aug	Sep	Oct	Nov	Dec	EOC
1.2	Engineering								
1.2.1	Calibration and Maintenance								
1.2.2	New Darkroom Facilities								
1.2.2.1	Design of Facilities								
1.2.2.2	Equipment Construction								
1.2.3	Shelf Life								
1.2.3.1	Overcoating								
1.2.3.1.1	Overcoating Equipment								
1.2.3.1.2	Material Search								
1.2.4	Red Lite								
1.2.4.2	Filter Tests								

Work Suspended

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1.3 PERKIN ELMER INTERFACE AND QC/QA

1.3.1 Perkin Elmer Interface

1.3.1.1 Plans and Progress of Perkin Elmer Program

The experimental plans detailed in the September 15 meeting at P.E. (see this section of the September Progress Report) were completed except for the laser RLD trial which was only a tentative item. The search for the optimum red lite filter for RLD (Item 1) has been completed. The R70 filter with a 5% cut-on at about 680 nm is optimum. It yields the fastest speeds and with good gammas at both room and elevated temperature. The use of narrow bandpass interference filters yielded approximately the same speeds and gamma at room and raised temperature respectively. The significance of these results is the fact that the interference filters can yield the same development with exceptionally low amounts of energy. This is a prime demonstration of the photochemical nature of the red lite development process.

Item 2, the determination of the RLD rate dependence, showed a definite break in the explosive vs. low gamma type development. RLD can only be speeded up to a certain point, beyond which the reaction takes off explosively yielding very steep gammas. In the experimental situation, which will be described in more detail in P.E.'s report, the developments from 4 minutes to 32 minutes yielded gammas from 1.7 to 2.0 and speeds that were at least as good or better. Developments of 2 minutes or shorter yielded the extremely high gammas of 5 to 10. The change in optimum development time was effected by use of ND filters. The lower gammas with long time development, correlate with the recent tests at [redacted] The red lite developed samples at P.E. appear very clean, and to the eye, appear as good as DPO samples!

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Item 3 was an attempt to establish a difference in the latent image dye product between the frozen/stored/shipped materials and the fresh materials. Because the frozen aged materials required an RLD filter cut-on approximately 10 nm further out than required by the fresh materials, the possibility existed that the absorption spectra of the latent image had also been shifted to longer wavelengths. The first conclusion from the spectra run on the stored frozen materials at P.E. show a latent image dye product peak at approximately the same wavelength as in the case of fresh materials (625 nm).

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A difference did appear in the spectra run on printout fixed material. A very good demonstration was presented that showed the film taking on a reddish hue with storage times from 4 to 18 days. The redder image indicates a higher proportion of D7, dye vs. D260 dye product. One possible cause would be acidification due to absorption of CO₂ in the film coating. Acidification, of course, would produce D7 dye in larger quantities. An attempt was made to avoid acidification by taking extra care to prevent CO₂ entering the box in which each of the film sheets was stored. The three sheets were boxed and sealed before frozen on the dry ice, and the seal was made with a heated platen to assure an air-tight bond. These three samples did not yield performance different from the other sheets of the same shipment. The possibility still exists that the polyethylene bags were permeable enough to allow sufficient quantities of CO₂ into the film box. The shift to redder image dye also correlates with previous results at [] The correlation might also be made with the fact that RLD with longer wavelengths than optimum may also yield a redder than "normal" image. Another factor that was discussed at the most recent meeting was the humidity of the air in which the film was stored. Although 40% relative humidity is "good" for room air in which the film is coated and processed, it might contain enough water to allow absorption into the film over longer periods of time, which probably would be detrimental to speed. The study of storage conditions for film is considered a priority item. This should tie in with the study to determine the cause of the lower RLD speeds at P.E.

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Item 4, the effect of raised temperature on development, was established conclusively. Amplification due to heat alone is marginal; a factor of two at most. Turning the red light on during the time the film is lying on the heated platen results in an additional amplification of 100. This series of tests was another indication that red light development is a photochemical process. A control test of red light development is valuable. As reported in the last progress report, the mobility of the chemicals, primarily the activator, is an extremely important factor for RLD.

The test goals laid out at the 16 October meeting have shifted the priorities of the original 9 August Interface program statement to adjust for the remaining time in the contract period. Top priority will be given to shipping overcoated material which will enable completion of Item 1 of the program statement. Item 2 has already been completed. Item 3, double development, will receive a lower priority although the ground work has already been laid. A thorough set of detailed

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instructions on plans for double development have been put together and sent to P.E. and the necessary RLD and interference filter background work has also been accomplished. The remaining time until the end of December probably will be sufficient to do a good job on overcoated materials as laid out in Items 1 and 4. Item 4, the determination of shelf life, will be the priority item for December. At that time we will combine the best materials and processing technology available at both laboratories and the tests will be carried out at both labs.

1.3.1.2 Test Planning for Perkin Elmer

QC/QA Interface has been able to accomplish some lab work while waiting for the new darkroom facilities to be completed. The primary accomplishment was to determine that elevated temperatures during RLD of fresh materials yields no advantage. Because of the success at Perkin Elmer with elevated temperatures during RLD we had hoped to see the same improvements in speed on fresh material as well. Our results reconfirm those of previous years. The prospects still remains, though, that room temperature storage of film may be improved in speed by heating film to 90°F during RLD. As pointed out in the above discussion of the most recent results from P.E., the mobility of the chemicals during RLD may be an important factor.

In a short series of tests to compare speeds with the Kodak 101 with the Horizons manufactured sensitometers, we show an indication that use of a black platen behind the film can result in a four-fold increase in speed. Further testing will be necessary to confirm this conclusion.

The three weeks of laboratory work by the QC/QA project team did succeed in training the new technician, so that significant testing can begin when the move to the new darkrooms is completed.

1.3.1.3 Liaison (Meetings)

The scheduled meeting with the consultants at [] took place on the sixteenth of October. The discussions with the consultants were considered fruitful by all concerned. The next meeting is scheduled tentatively sometime during the first half of December, which will provide the last opportunity for an

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input in this contract period. P.E. will request involving the consultants in a small amount of lab work at their respective facilities. The lab work at P.E. is being reserved exclusively for the original goals as discussed in Section 1.3.1.1 of this report. The next scheduled meeting on this portion of the interface program is for the latter part of November when the final plans will be made for testing optimum shelf life results.

1.3.1.4 Film Shipment

<u>Shipment Number</u>	<u>Date</u>	<u>No. of Sheets</u>	
11	14 August	15	Received
12	28 August	5	Received
13	11 September	15	Received
14	24 October	5	
15	6 November	15	
16	4 December	15	

The last two shipments, 15 and 16, will be overcoated film of Formula 10. The reasons for the switch to Formula 10 at [] is discussed in the chemistry section. The switch to Formula 10 for the interface program will keep the work at P.E. most relevant to the 325 program. Because Shipment 15 will involve two changes, the formula and overcoat, Shipment 14 will be made up of a small number of sheets of non-overcoated Formula 10. This is necessary and should be sufficient to separate the causes for any changes in performance of the overcoated Formula 10 film material.

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1.3.2 QC/QA

1.3.2.1 Materials Inventory

Sufficient quantities for the larger coating effort have been maintained. The following photograde quantities were available as of 15 October 1972.

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	<u>gm/ml Available</u>	<u>Handcoating Equivalent Amounts (Formula 5/D7)</u>
D260:	82	1,800
D7:	350	12,300
CBr ₄ :	1,378 1,500 ml	3,600
4PO:	100 1,500 ml	12,500
D8	110	

1.3.2.2 Calibrations

The quality of Formula 5/D7 materials continues to be maintained at a sufficient level. The calibration of sensitometers and RLD units have been maintained on a weekly basis without any problem. The new sensitometers will be cross-calibrated with the old sensitometers using silver film if time permits. The basic design of the new sensitometer is a condensation of the through-the-base design for the original set of four sensitometers for 325. The QC check of the polyester base thickness continues to be made on a weekly basis. The flatness of the base continues to be poor as reported in the last monthly report. Free samples have been elicited from Gevaert in Mortsel, Belgium, which should be available in November. New coating plates have been made for most of the coating stations which include an inlaid optical flat glass. This will be superior to the metal plates, which have become distorted through several years usage. The manufacturer has specified the flatness to be within .02 mils. We have measured them to be at least as good as .5 mils, which is more than sufficient considering the base polyester which is being used on project.

1.3.2.3 Clean Room Standards

More rigorous clean room procedures are now being followed in the hand coating areas. The wearing of cover garments is universally observed. General clean-up is on a daily basis. Use of disposable paper lab coats, booties and hats has been

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terminated because of the lint problem. Heavily starched cloth garments are being used with shoes that are used only in the lab area.

Microscopic inspection of dust samples revealed that they were mostly lint, and the lint often had microscopic sized crystals of dye attached to or impregnated in it. Chemical analyses of dust samples and filter samples showed sporadic traces of PO, D7, and D260. Analyses of non-Formula 5/D7 materials were not done. Extensive work on the spreading spot problem with stored overcoated materials showed that the seed crystals are at least one of the causes. Seed crystals are inherent in the atmosphere of chemical labs. The present controlled environment rooms are a big improvement over previous labs, but not a substitute for class A type clean rooms.

The dye purification lab now has a full sized Barnebey Cheney air purification unit. The dust filters in each of the Barnebey Cheney units will be switched to the "viscosine" hexachlorophene impregnated furnace dust filters, which have proven to be better traps for the airborne D260 crystals.

1.3.2.4 Standard Material Purifications

1.3.2.4.1 D260

The purification of the D259 intermediate results in considerably higher quality D260. The purification of the Michler's hydrol intermediate was optimized at H.R.I. in January, 1972, and the details were transmitted to ChemSampCo, the current supplier of our crude D260. The Michler's hydrol is recrystallized from a benzene/pet ether solution. A double recrystallization from this medium serves to remove TMB completely as tested by TLC.

D260 is recrystallized by dissolving in hot benzene under red light and adding methanol while still hot. Cooling gives white crystals which are filtered and dried under vacuum. The crystals are ground in a mortar and pestle and dried under vacuum. This purification procedure will now be considered the primary initial procedure for all D260 received from ChemSampCo provided the quality of the crude received remains constant as monitored by TLC.

Shipments of D260 from ChemSampCo consist of light blue material which was exceedingly clean by TLC, containing

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only a trace of anthrone (less than 0.001%). For TLC crude D260 is eluted on a dry basic alumina column, activity grade III, using 95/5 benzene/ethyl acetate in complete darkness except for a red flashlight. For QC TLC plates are spotted in the dark and should indicate only a trace of anthrone present.

The anthrone impurity gives a single intensely fluorescent spot when examined by TLC on alumina. The infrared spectrum of a concentrated sample is essentially identical to the infrared spectrum of 2,7-bis(dimethylamino)-9,9-dimethylantrone which had been prepared recently in these laboratories and had been a suspected impurity in crude D260.

While the anthrone was not determined to be deleterious to film performance, the closely associated DMAP was. A one-to-one relationship was established between the anthrone and the DMAP, which is much more difficult to detect in a routine QC check. The relationship was established by dissolving a sample of D260 in benzene and placed in a quartz UV cell and irradiated with UV light. After 4 hours, p-dimethylaminophenol could be detected by TLC at a concentration of about 1/100%. The solution was diluted to a concentration of 1/100 that of the original. Anthrone was detected in this solution at a concentration of about 1/10,000% by TLC. From this it was concluded that the phenol and anthrone were present in about equal concentrations.

Thin layer chromatographic examination of the D260 delivered to us in January, 1972, by ChemSampCo revealed a gross impurity eluting just ahead of the D260. The impurity was definitely established as deleterious photographically as reported in December, 1972. Elemental analysis of this impurity was correlated with infrared spectral data and physical properties in January, 1972, and this material was identified as N,N,N',N'-tetramethylbenzidine (TMB). This compound no doubt arises by oxidative coupling of dimethylaniline in the preparation of Michler's hydrol and is carried through unreacted in the synthesis of D260. Work in January, 1972, showed that the best way to remove this impurity is by several triturations in hot ethanol in which D260 is only sparingly soluble. It was discovered that practically all of the TMB can be removed in this way by one alcohol trituration of material prepared in our laboratories, provided the Michler's hydrol had gone through at least one cyclohexane recrystallization prior to use in D260 synthesis.

Analysis of mass spectral data of various samples of D260 has revealed a condensation product impurity. At 250°C scan temperature, a relatively large peak appears at M/e 666 in

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some samples, notably a crude sample and a particularly good photograde sample. The difference between M/e 666 and M/e 413 (D260) turns out to be M/e 253 (100% peak for Michler's hydrol). This leads immediately to the very real possibility that the 666 contaminant is in fact a condensation product of D260 and Michler's hydrol arising from the carry-over of Michler's hydrol from D259 synthesis. This M/e would in fact be 665 but it is quite possible that instrument error this far out might account for this small difference.

1.3.2.4.2 Other Chemicals

Benzene: On warming D7 in reagent grade benzene or reagent grade benzene containing polystyrene, an orange-red color develops nearly instantaneously indicating dye formation. On the other hand, treatment of reagent grade benzene by shaking successively with concentrated H_2SO_4 , water, NaOH solution, water and then drying over molecular sieve results in benzene which, when heated to the boil with D7, produces only a slight change in color. It is now our plan to distil from sodium wire benzene which has been treated in this way and freeze-dry the resulting distillate to obtain ultrapure benzene for use in film studies.

4PO: Practical grade 4PO is recrystallized from acetone/petroleum ether by the usual procedure. This white solid is then transferred to a Labconco glove box where it is recrystallized twice from benzene which has been pretreated by base and water washes and then stored over a molecular sieve. The twice recrystallized 4PO is placed in a vacuum desiccator over P_2O_5 and pumped on for two days.

CBR_4 : Analysis of photographically good and bad samples of CBR_4 by TLC was unexpectedly successful in short order. Elution was carried out on J.T. Baker almmina 1B-F using an isomeric mixture of hexanes. The chromatogram (colorless) was then developed by spraying with photograde D260 dissolved in cyclohexane followed by irradiation with a UV lamp. Photo-inferior (white) CBR_4 showed the presence of a significant impurity resolved just behind the main spot. A number of samples were checked and cross-checked by film evaluation with consistent results. Samples showing one spot are acceptable while all those showing the presence of impurity are photographically bad.

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1.3	Perkin Elmer Interface and QC/QA	DOC	Jul	Aug	Sep	Oct	Nov	Dec	EOC
1.3.1	Perkin Elmer Interface								▽
1.3.1.2	Test Planning for Perkin Elmer								
1.3.1.3	Liaison (Meetings)		▽ ▽	▽ ▽	▽	▽	▽		
1.3.1.4	Film Shipments			▽ ▽	▽	▽	▽	▽	
1.3.2	QC/QA								▽

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PROBLEMS

1. Securing best quality polyester base material.
2. Obtaining 70°F working temperature in oxygen-free coating test chamber.

PLANS FOR NEXT REPORTING PERIOD

1. Continue screening of decay inhibitors.
2. Enlarge effort to integrate all approaches to extending shelf life.
3. Expand shelf life evaluation studies.

FINANCIAL

The following figures cover the Financial Status for the project through September 30, 1972.

The present underrun reflects some delays in staffing and in fabrication of facilities. The higher level of expenditures expected during the next three month period should bring the cost-at-completion close to the original plan.

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Next 5 Page(s) In Document Denied

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